Supporting Data

Structure-Activity Relationships inTLR2-agonistic Diacylthioglycerol Lipopeptides

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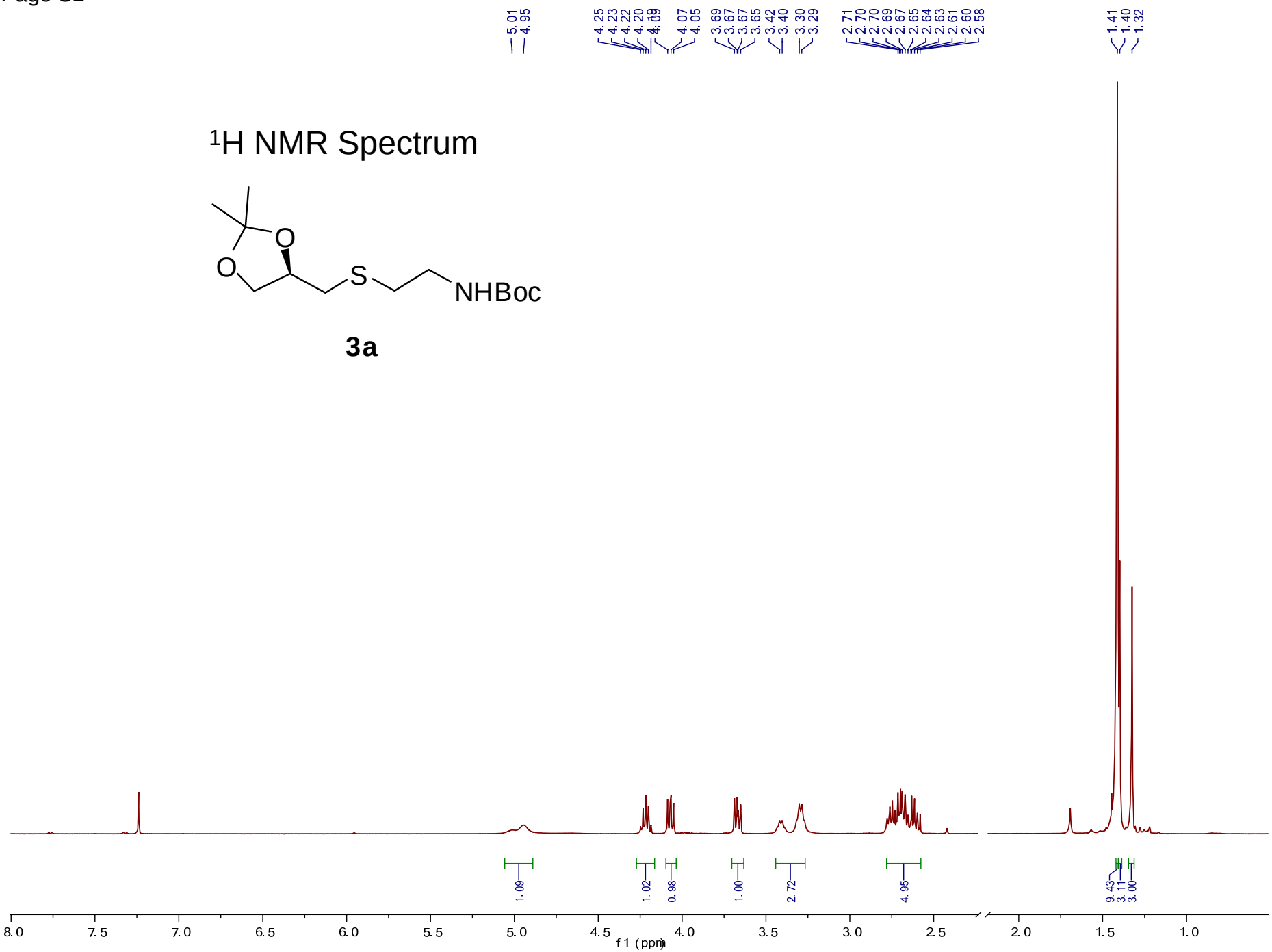
^{1}H, ^{13}C NMR, and Mass-Spectral Data
of all key intermediates and final compounds

^{1}H NMR Spectrum

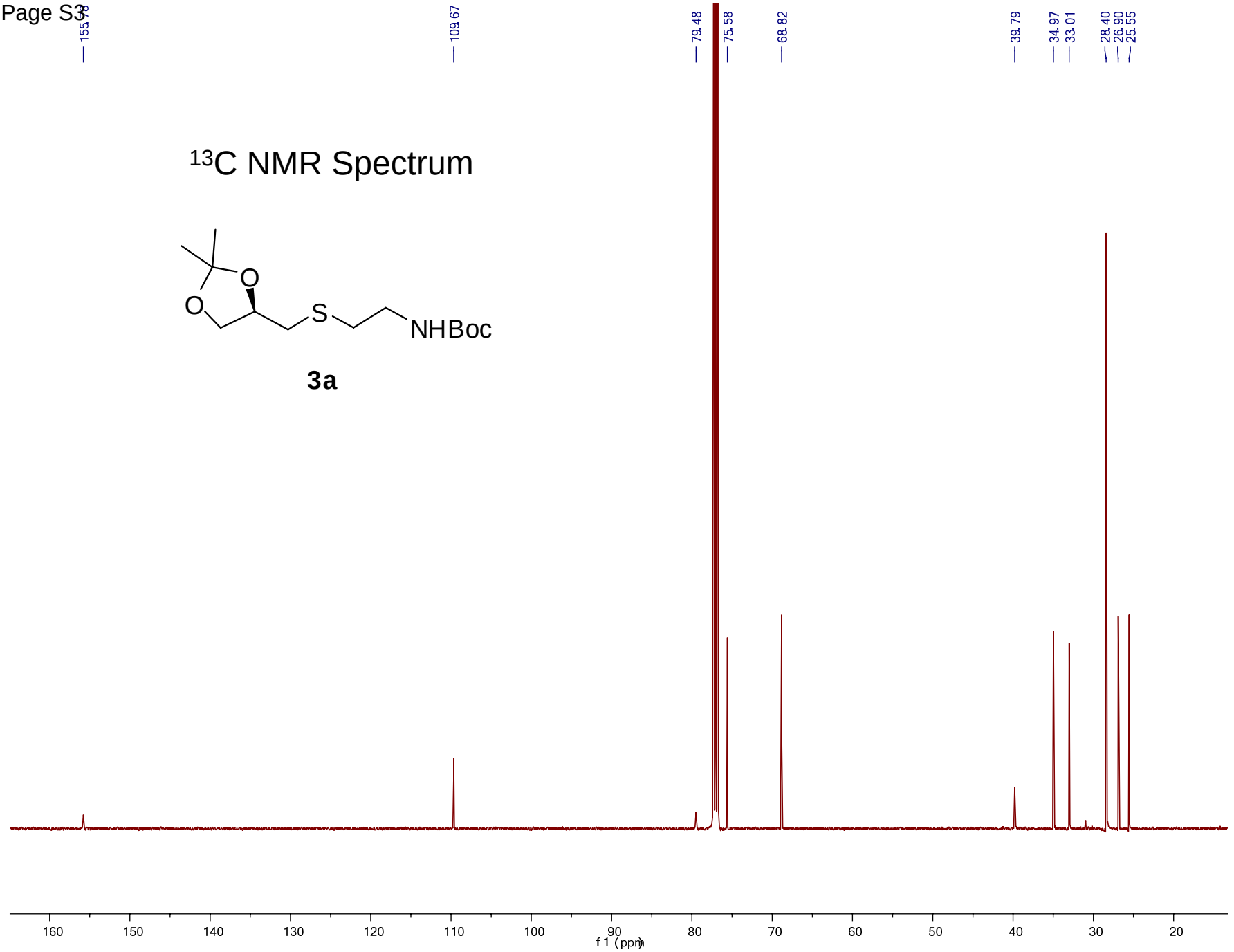
3a



155.78
109.67
79.48
75.58
68.82
39.79
34.97
33.01
28.40
26.90
25.55

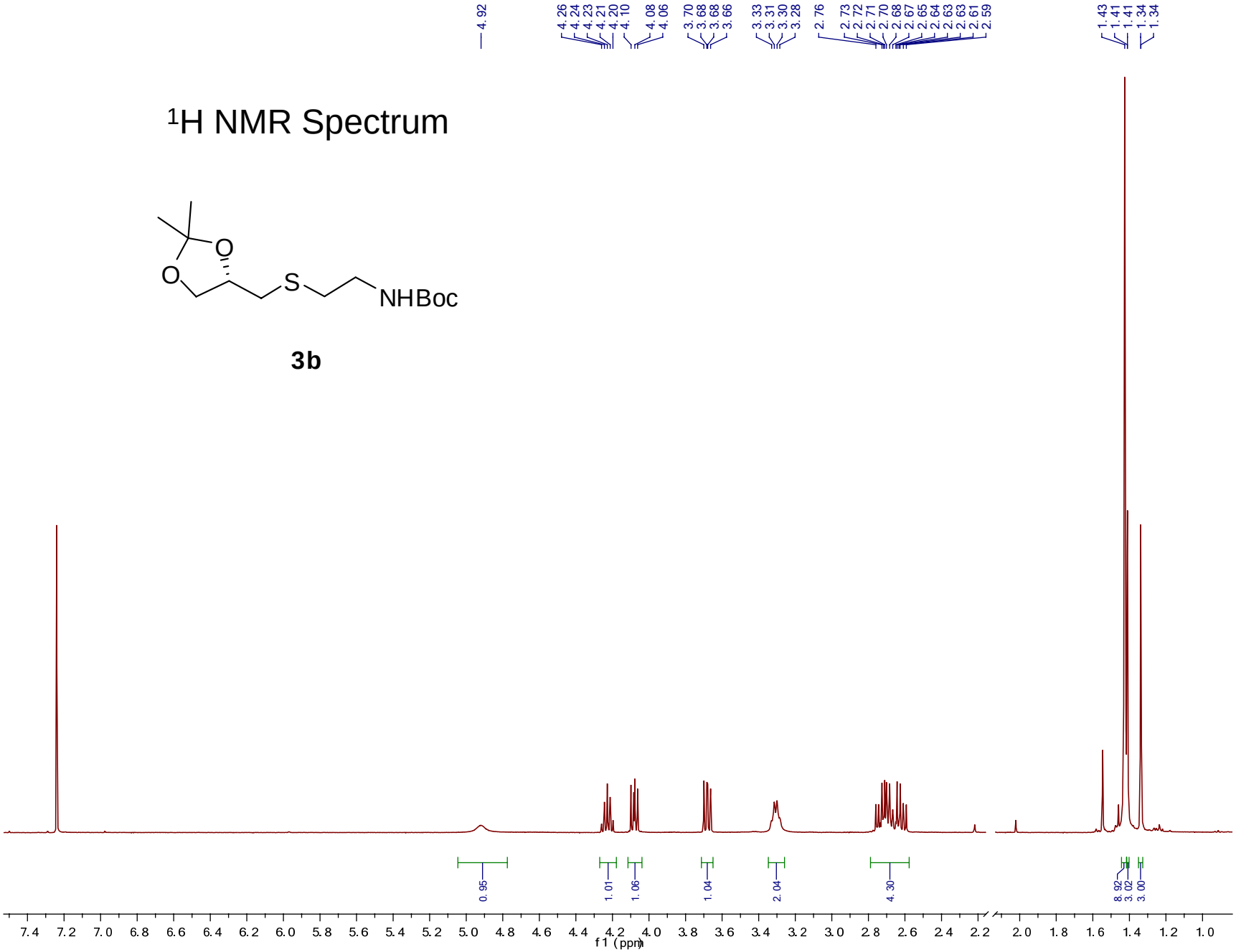
^{13}C NMR Spectrum

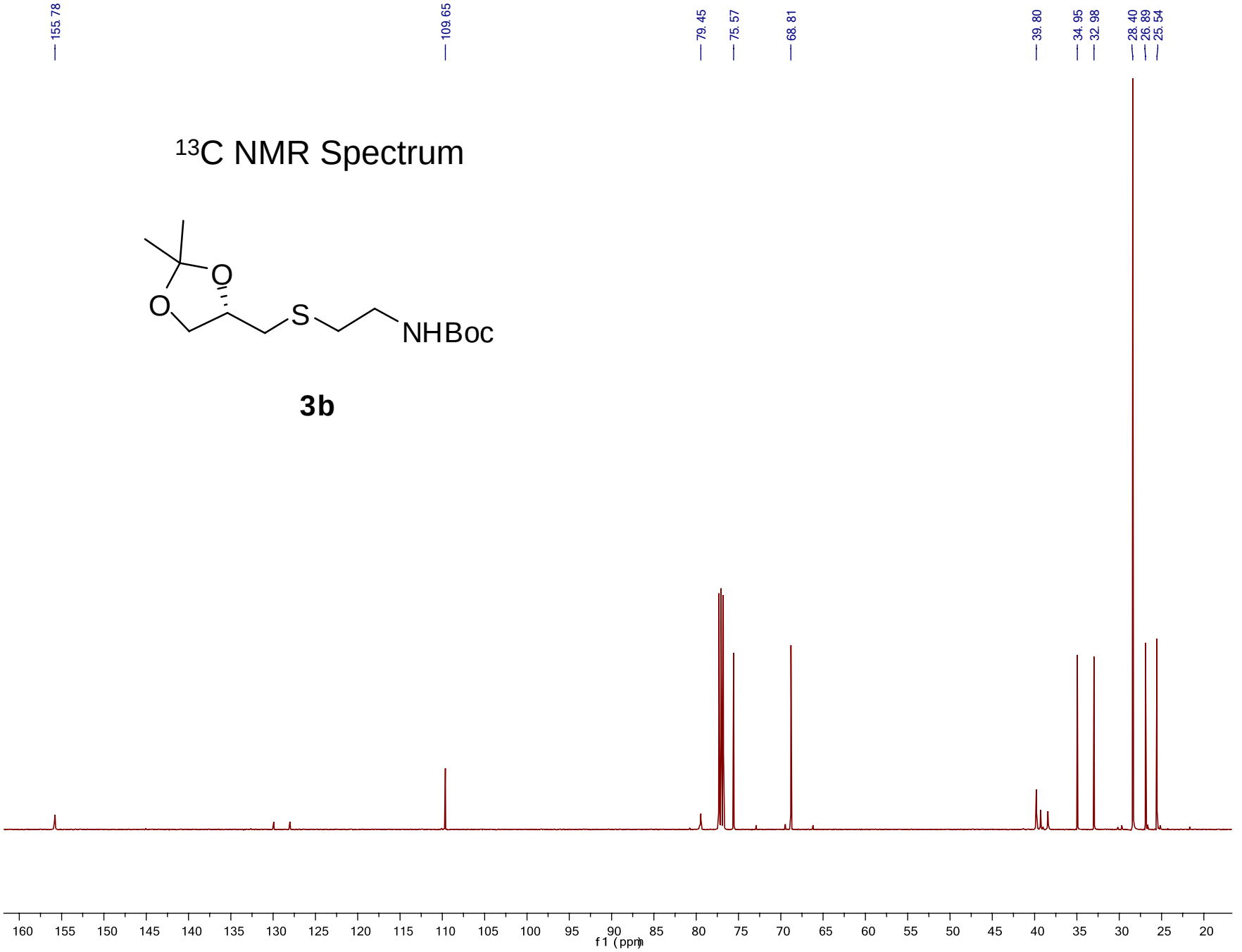
3a

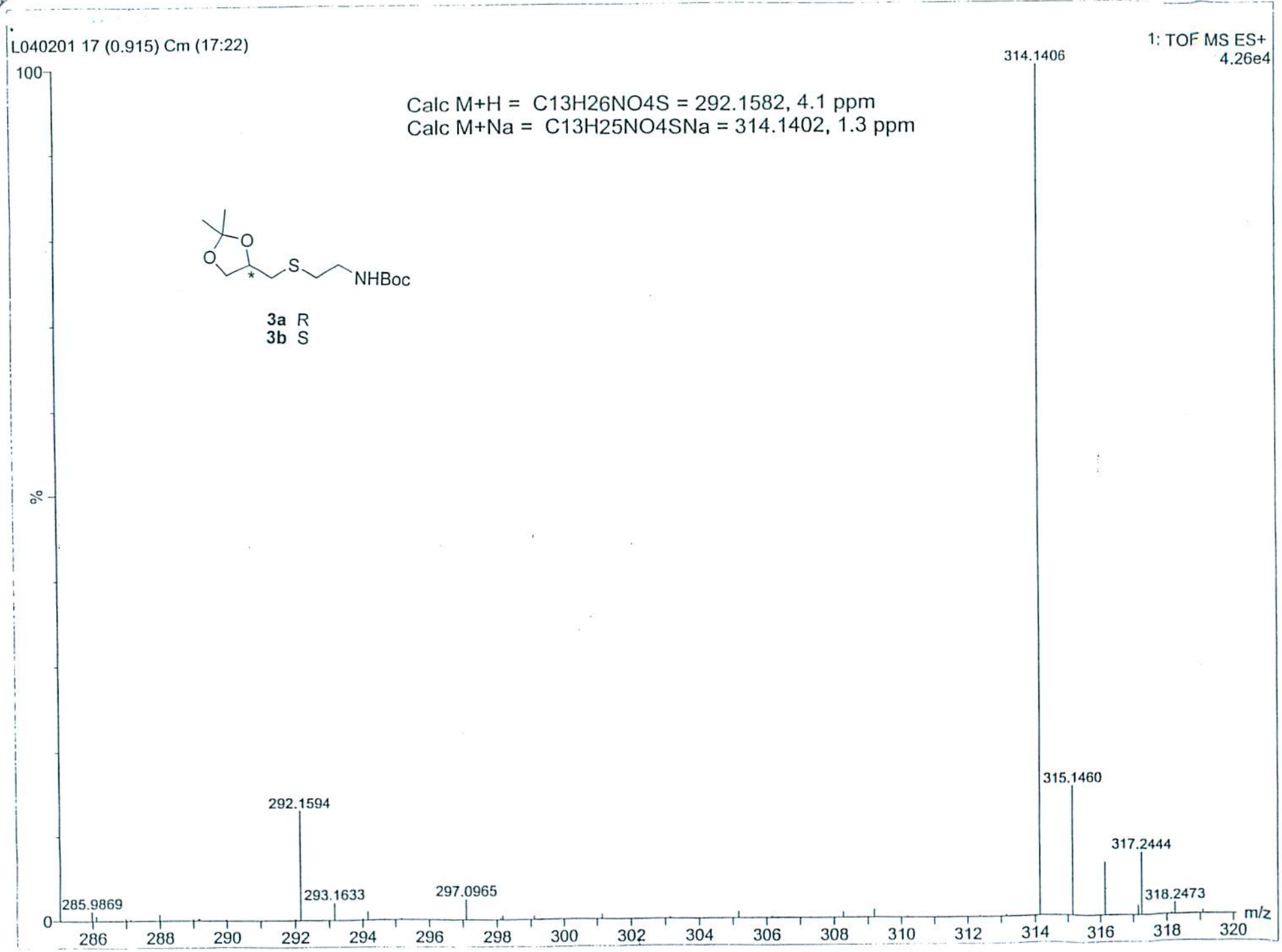


^{1}H NMR Spectrum

3b

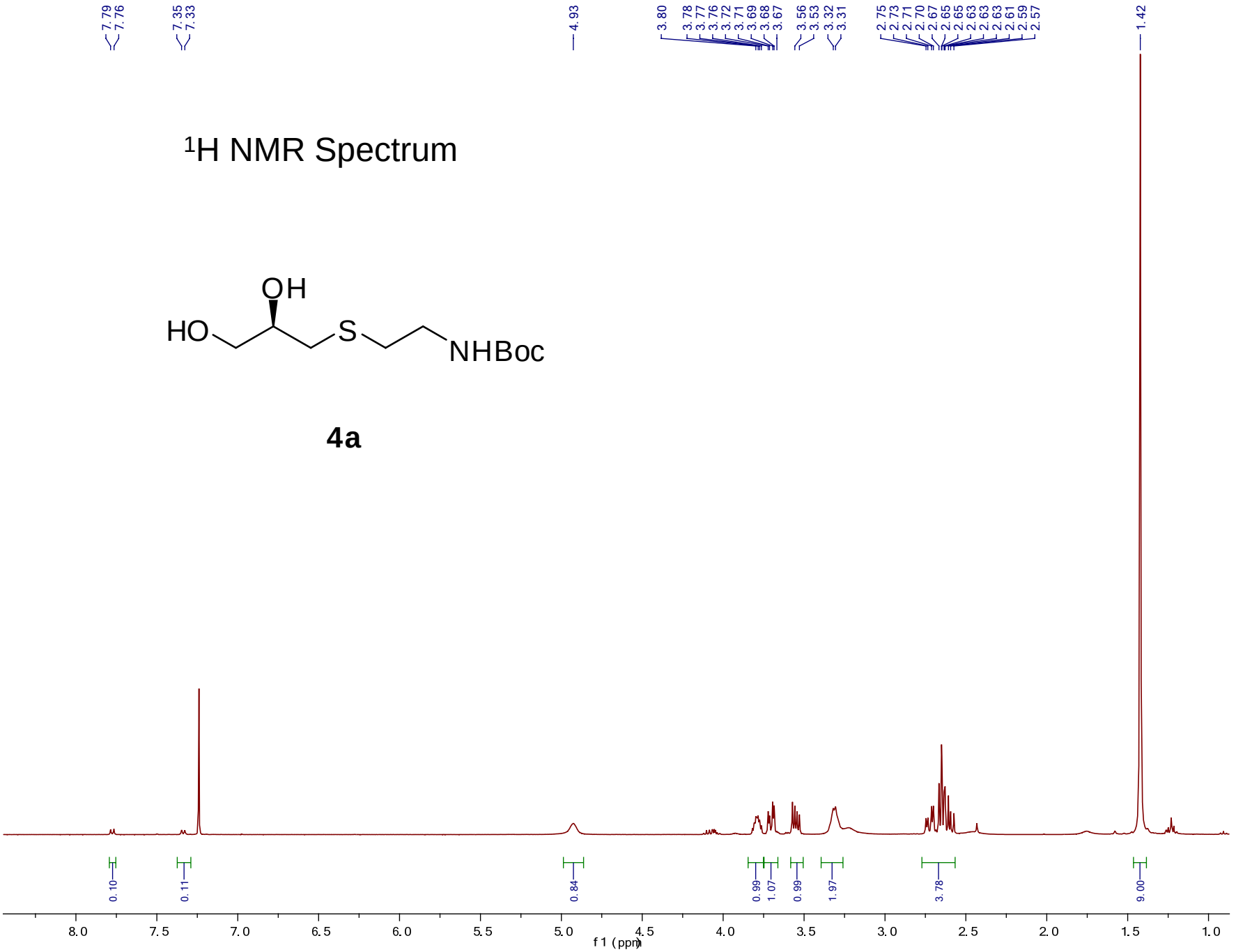


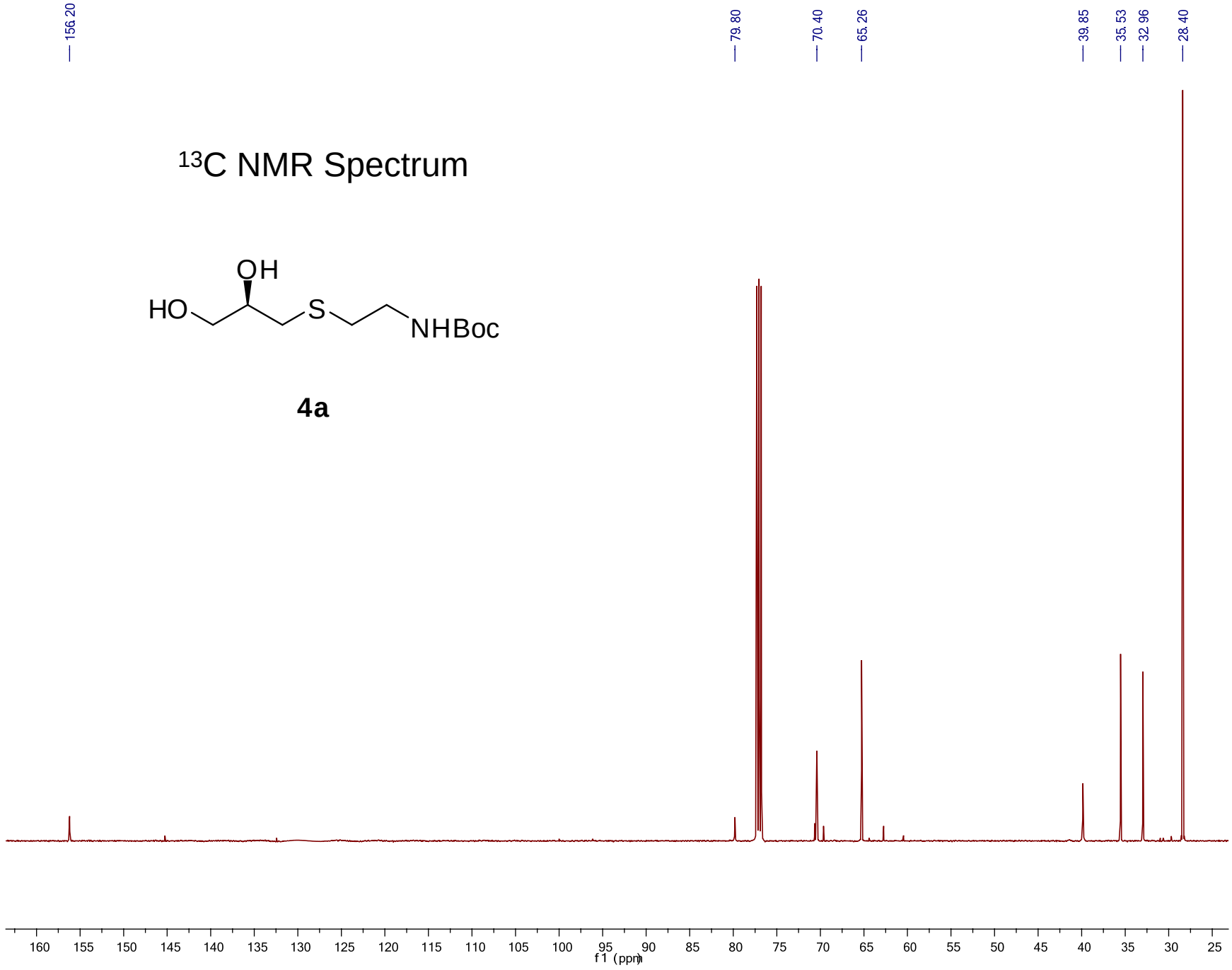

155.78
109.65
79.45
75.57
68.81
39.80
34.95
32.98
28.40
26.89
25.54
13C NMR Spectrum
O
O
S
NHBoc
3b
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)

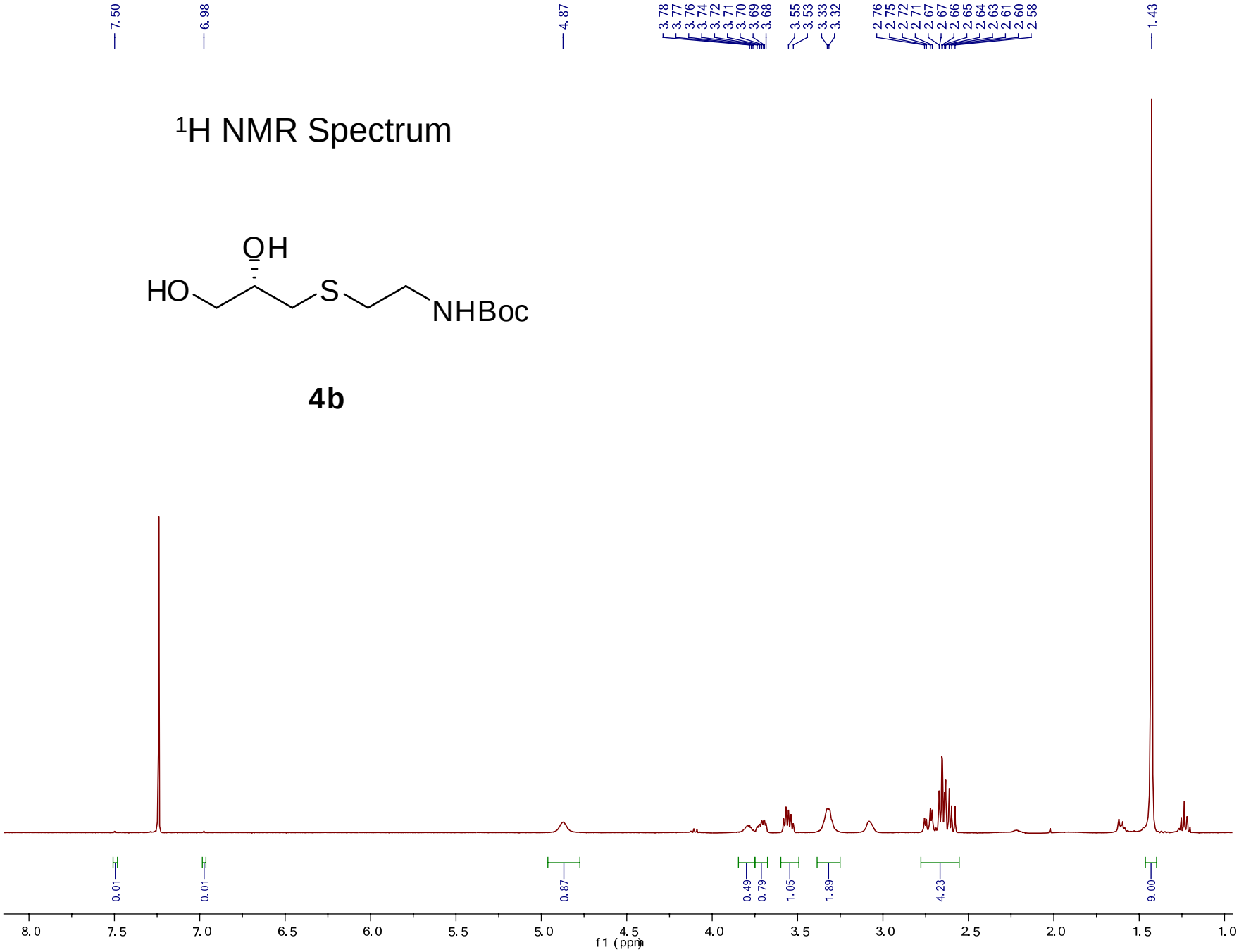

L040201 17 (0.915) Cm (17:22)
1: TOF MS ES+
4.26e4
100
%
0
Calc M+H = C13H26NO4S = 292.1582, 4.1 ppm
Calc M+Na = C13H25NO4SNa = 314.1402, 1.3 ppm
O
O
S
NHBoc
*
3a R
3b S
314.1406
315.1460
317.2444
318.2473
292.1594
293.1633
297.0965
285.9869
m/z
286
288
290
292
294
296
298
300
302
304
306
308
310
312
314
316
318
320

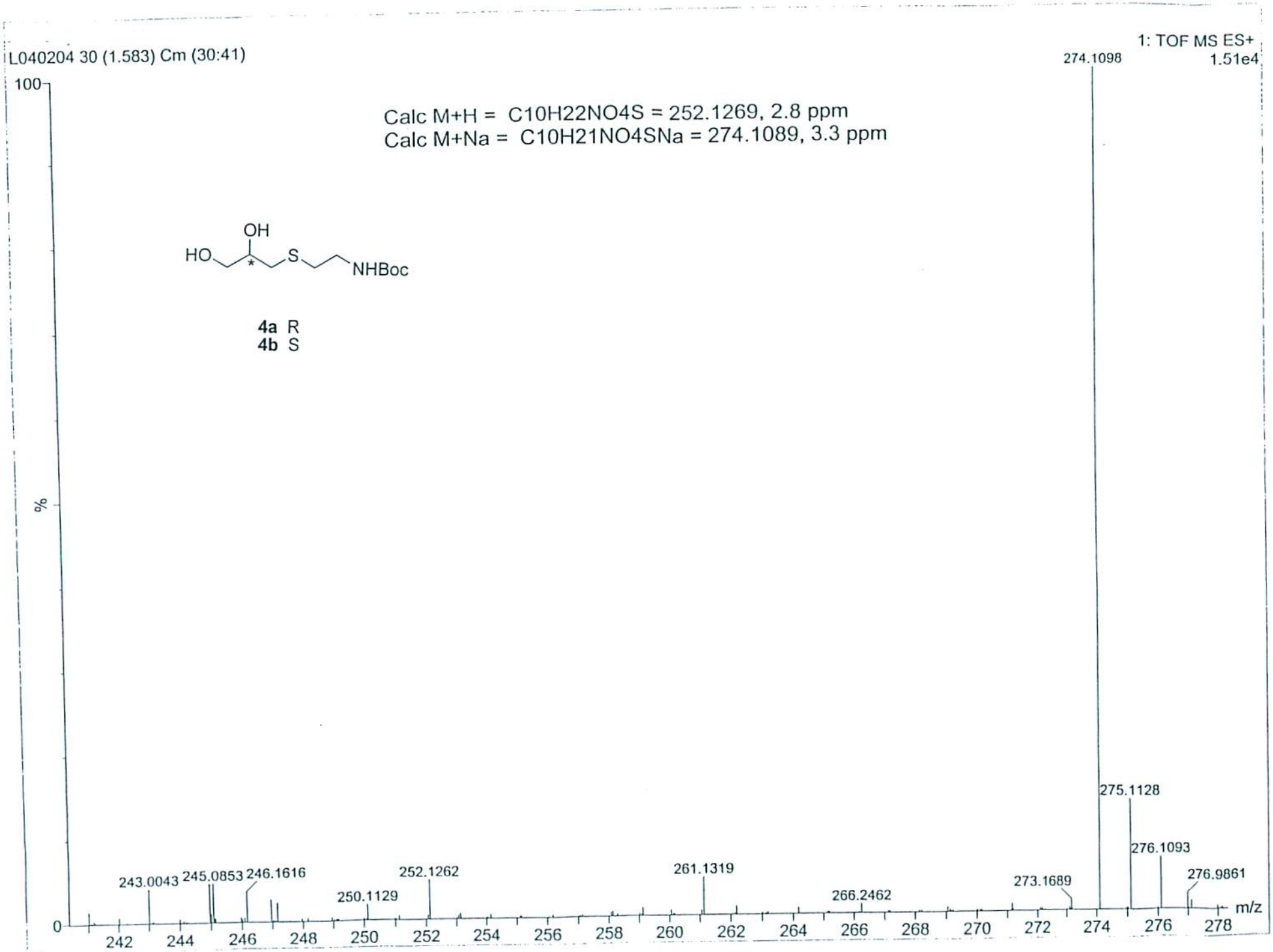
^{1}H NMR Spectrum

4a



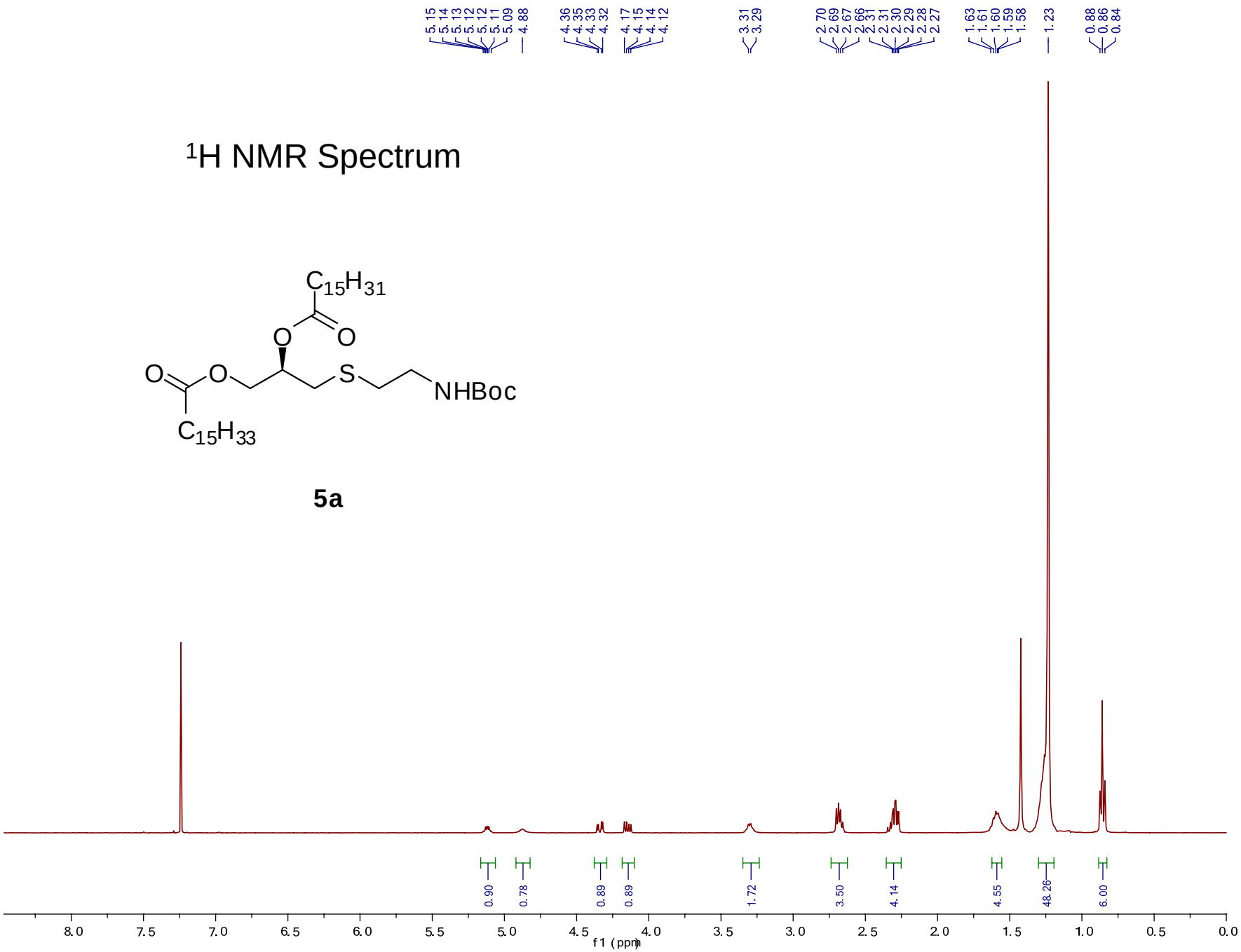

156.20
79.80
70.40
65.26
39.85
35.53
32.96
28.40
13C NMR Spectrum
OH
HO
S
NHBoc
4a
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25
f1 (ppm)

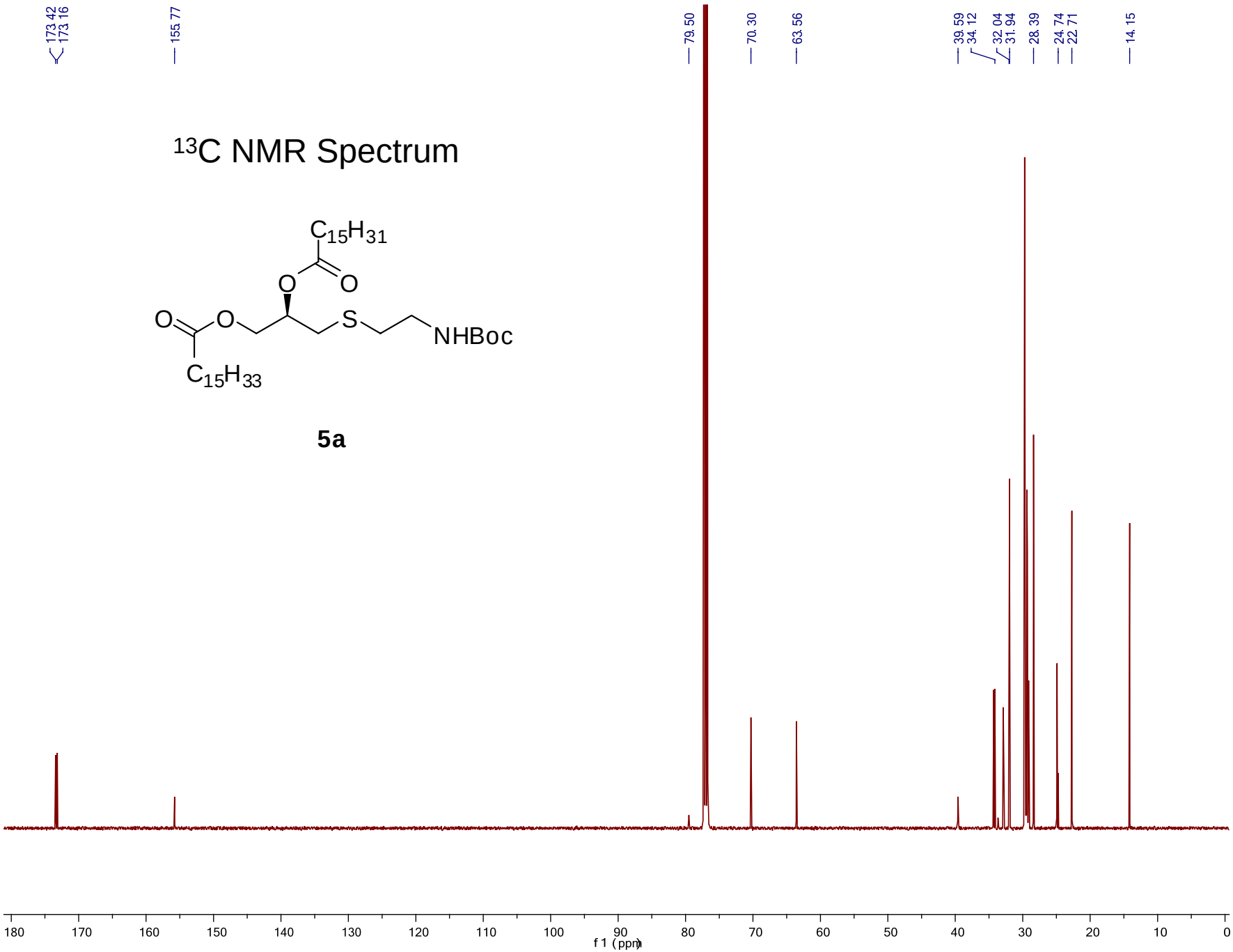

7.50
6.98
4.87
3.78
3.77
3.76
3.74
3.72
3.71
3.70
3.69
3.68
3.55
3.53
3.33
3.32
2.76
2.75
2.72
2.71
2.67
2.67
2.66
2.65
2.64
2.63
2.61
2.60
2.58
1.43
1H NMR Spectrum
OH
HO
S
NHBoc
4b
0.01
0.01
0.87
0.49
0.79
1.05
1.89
4.23
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


L040204 30 (1.583) Cm (30:41)
1: TOF MS ES+
1.51e4
100
%
0
Calc M+H = C10H22NO4S = 252.1269, 2.8 ppm
Calc M+Na = C10H21NO4SNa = 274.1089, 3.3 ppm
OH
HO
S
NHBoc
4a R
4b S
274.1098
275.1128
276.1093
276.9861
273.1689
266.2462
261.1319
252.1262
250.1129
243.0043
245.0853
246.1616
m/z
242
244
246
248
250
252
254
256
258
260
262
264
266
268
270
272
274
276
278

^{1}H NMR Spectrum

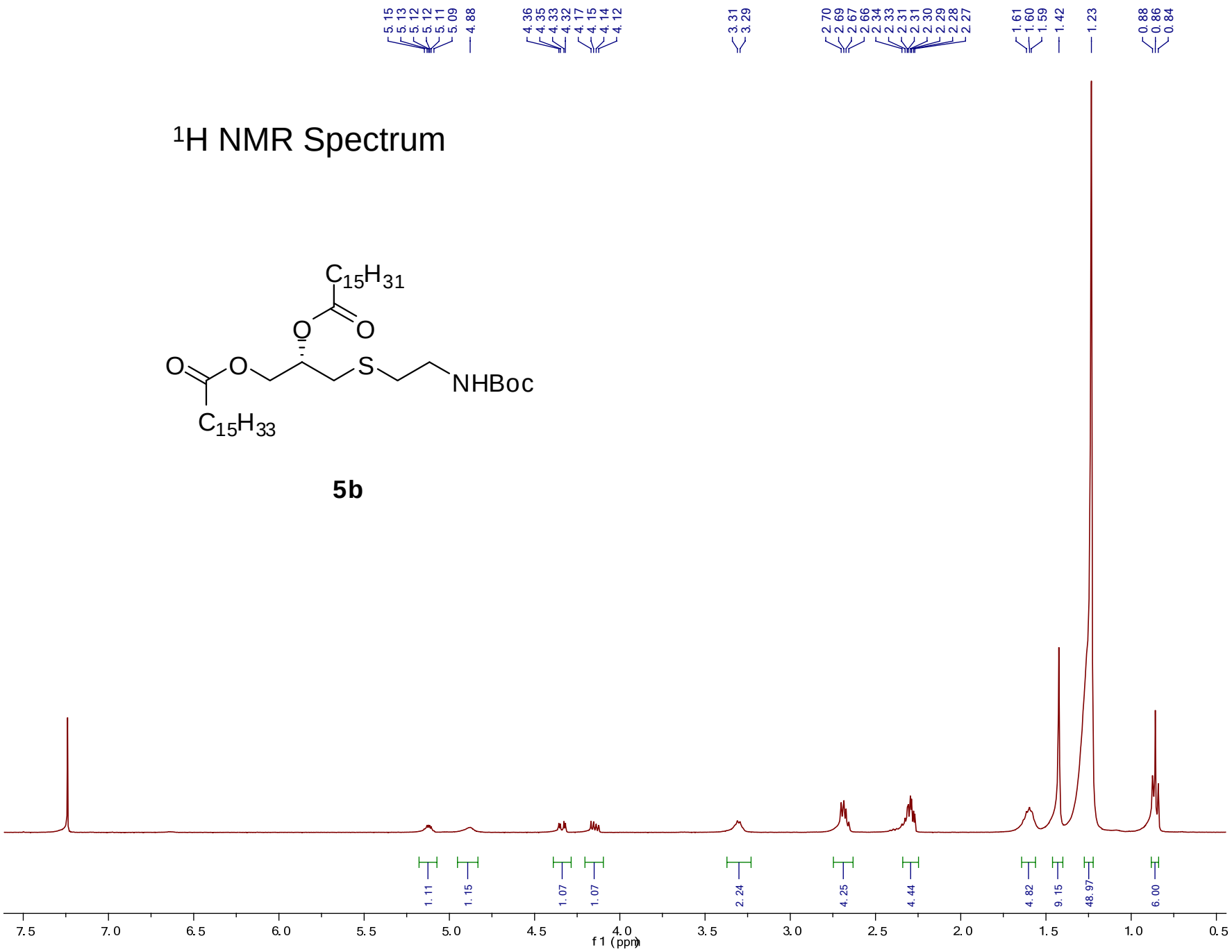
5a

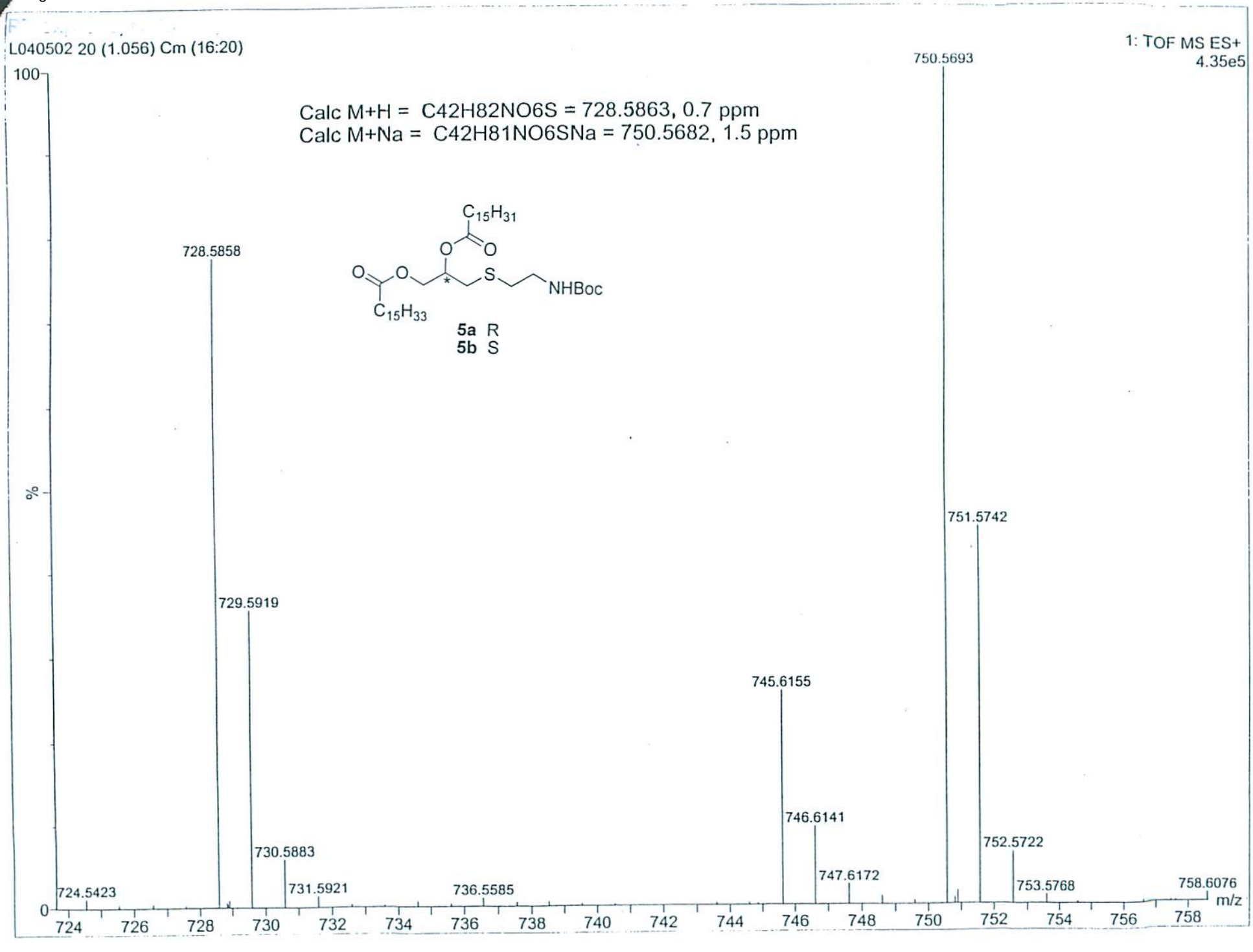



173.42
173.16
155.77
79.50
70.30
63.56
39.59
34.12
32.04
31.94
28.39
24.74
22.71
14.15
13C NMR Spectrum
C15H31
O
O
O
O
S
NHBoc
C15H33
5a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{1}H NMR Spectrum

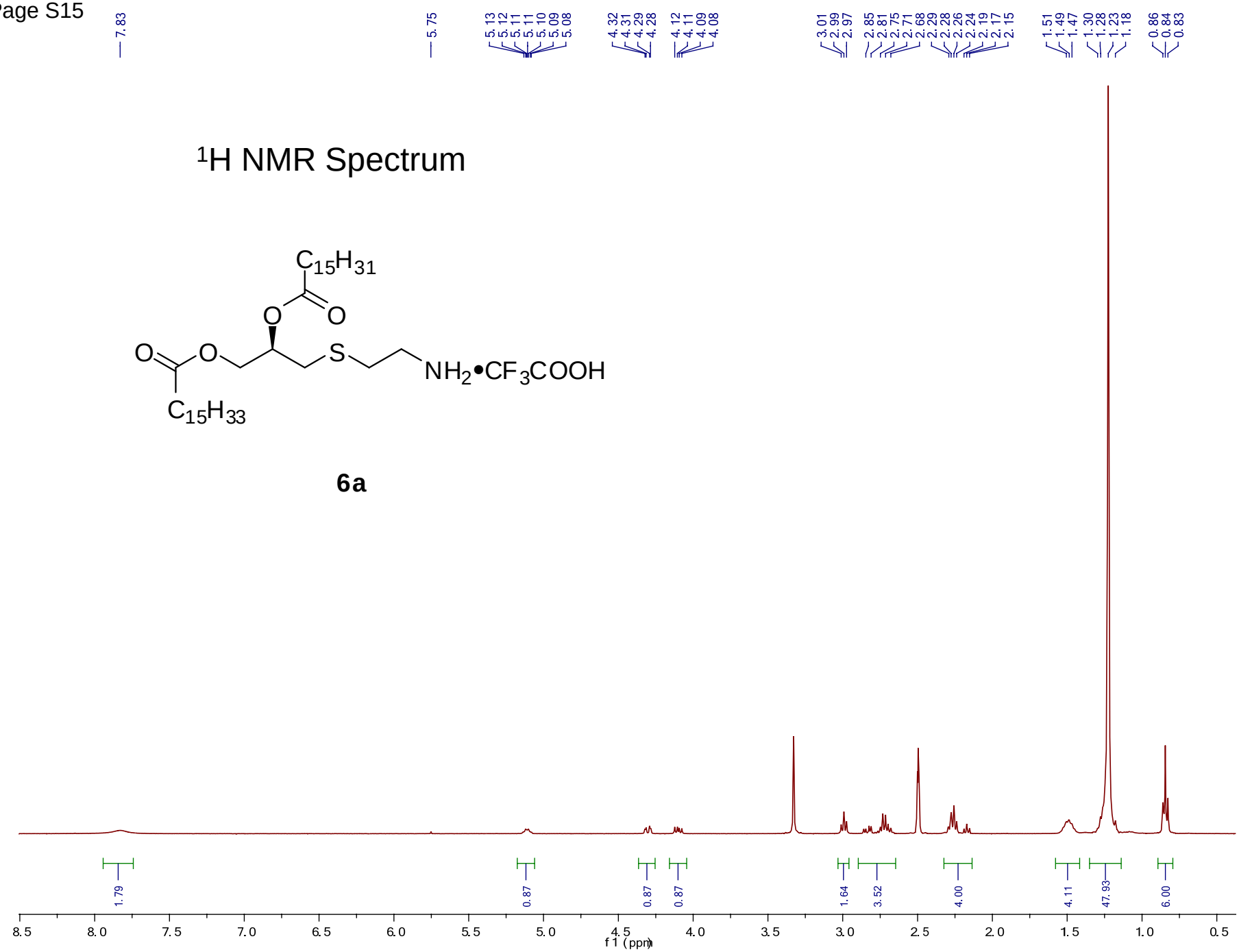
5b




L040502 20 (1.056) Cm (16:20)
1: TOF MS ES+
4.35e5
Calc M+H = C42H82NO6S = 728.5863, 0.7 ppm
Calc M+Na = C42H81NO6SNa = 750.5682, 1.5 ppm
C15H31
C15H33
NHBoc
5a R
5b S
100
%
0
m/z
728.5858
729.5919
730.5883
731.5921
724.5423
736.5585
745.6155
746.6141
747.6172
750.5693
751.5742
752.5722
753.5768
758.6076
724
726
728
730
732
734
736
738
740
742
744
746
748
750
752
754
756
758

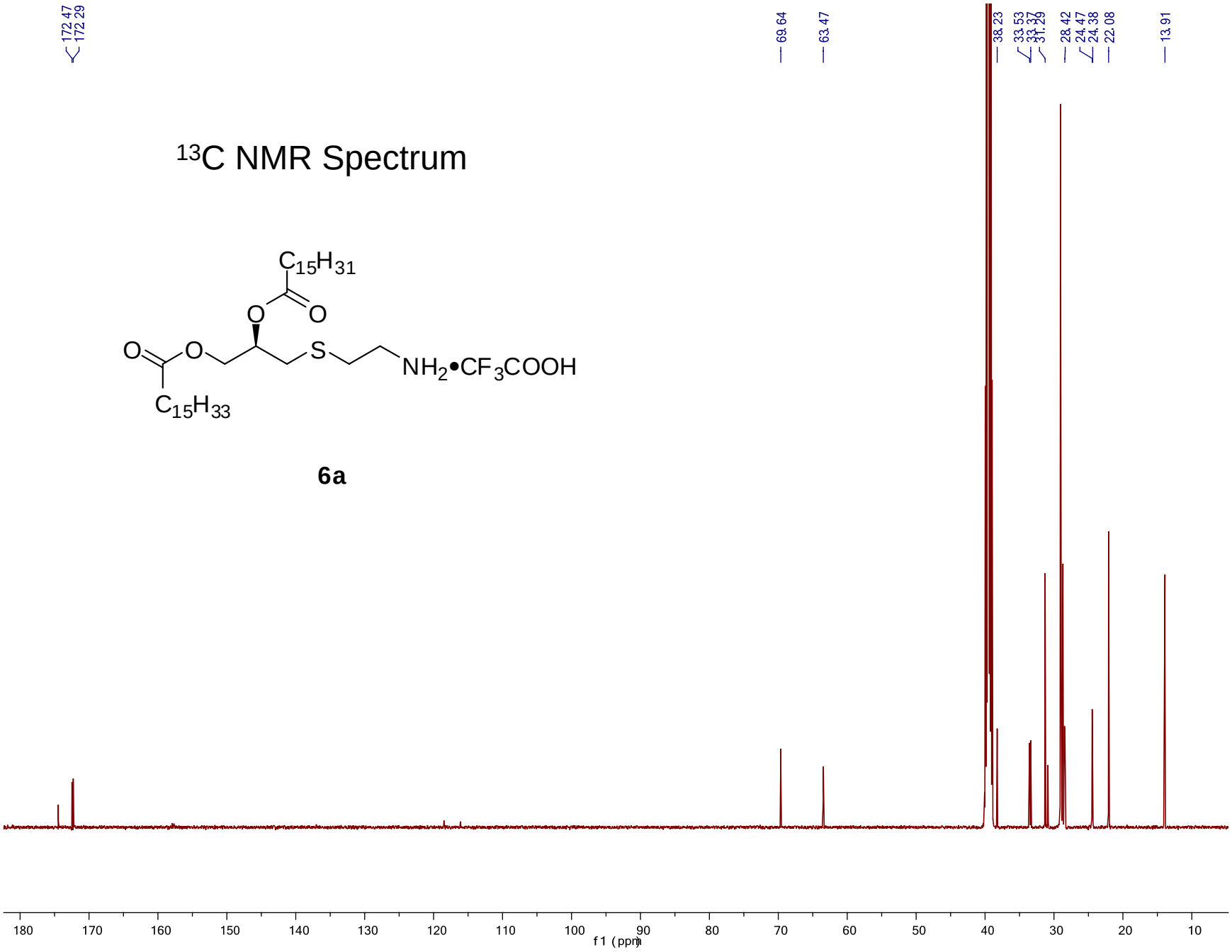
^{1}H NMR Spectrum

6a



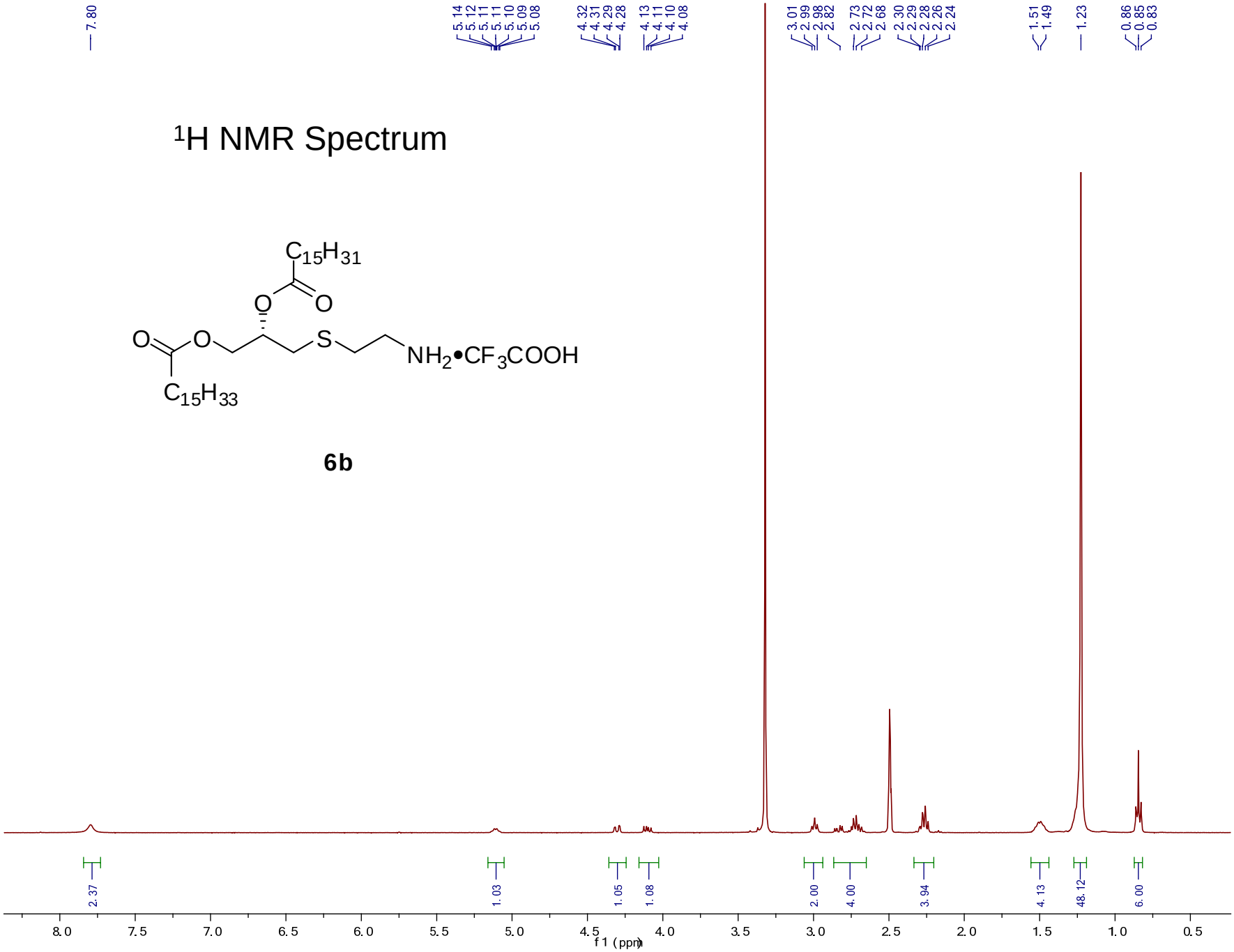
^{13}C NMR Spectrum

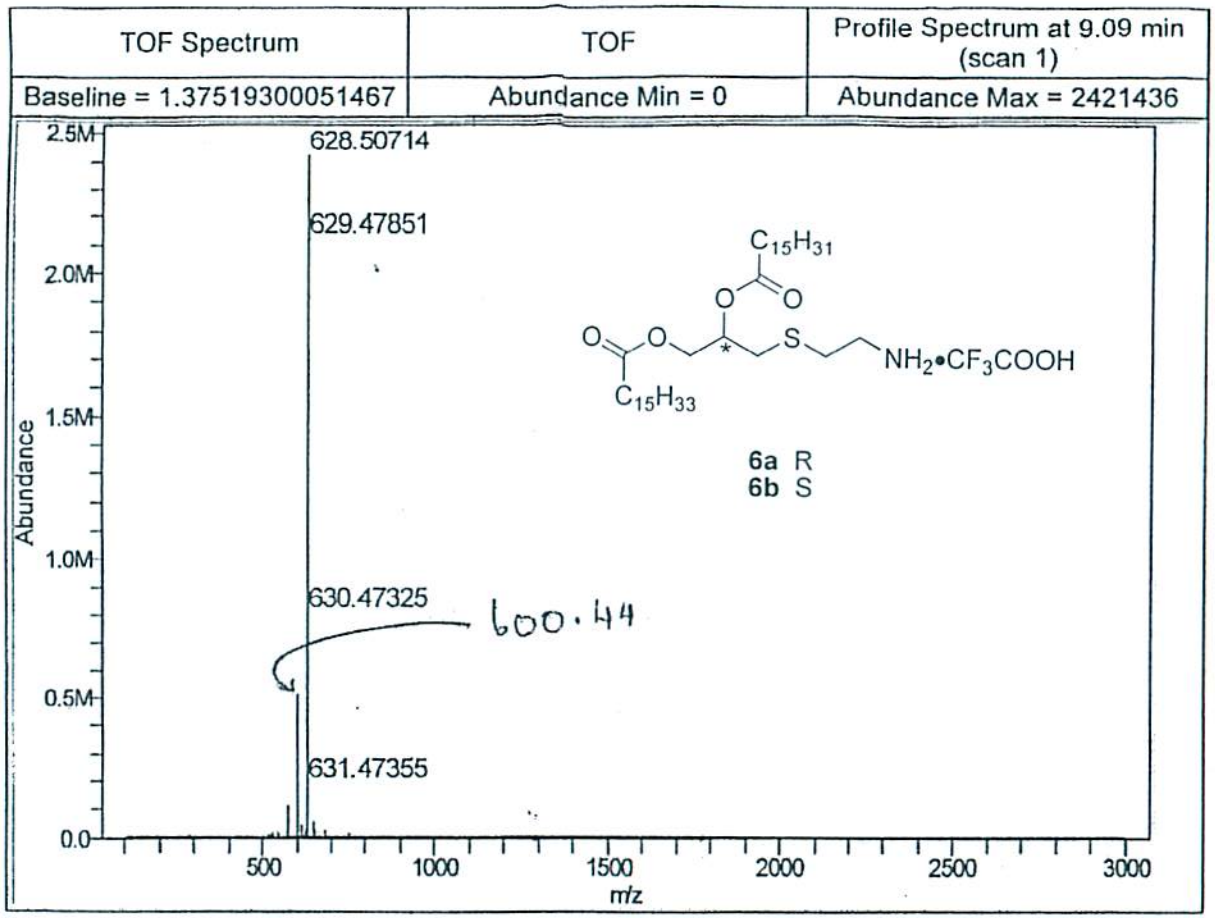
6a

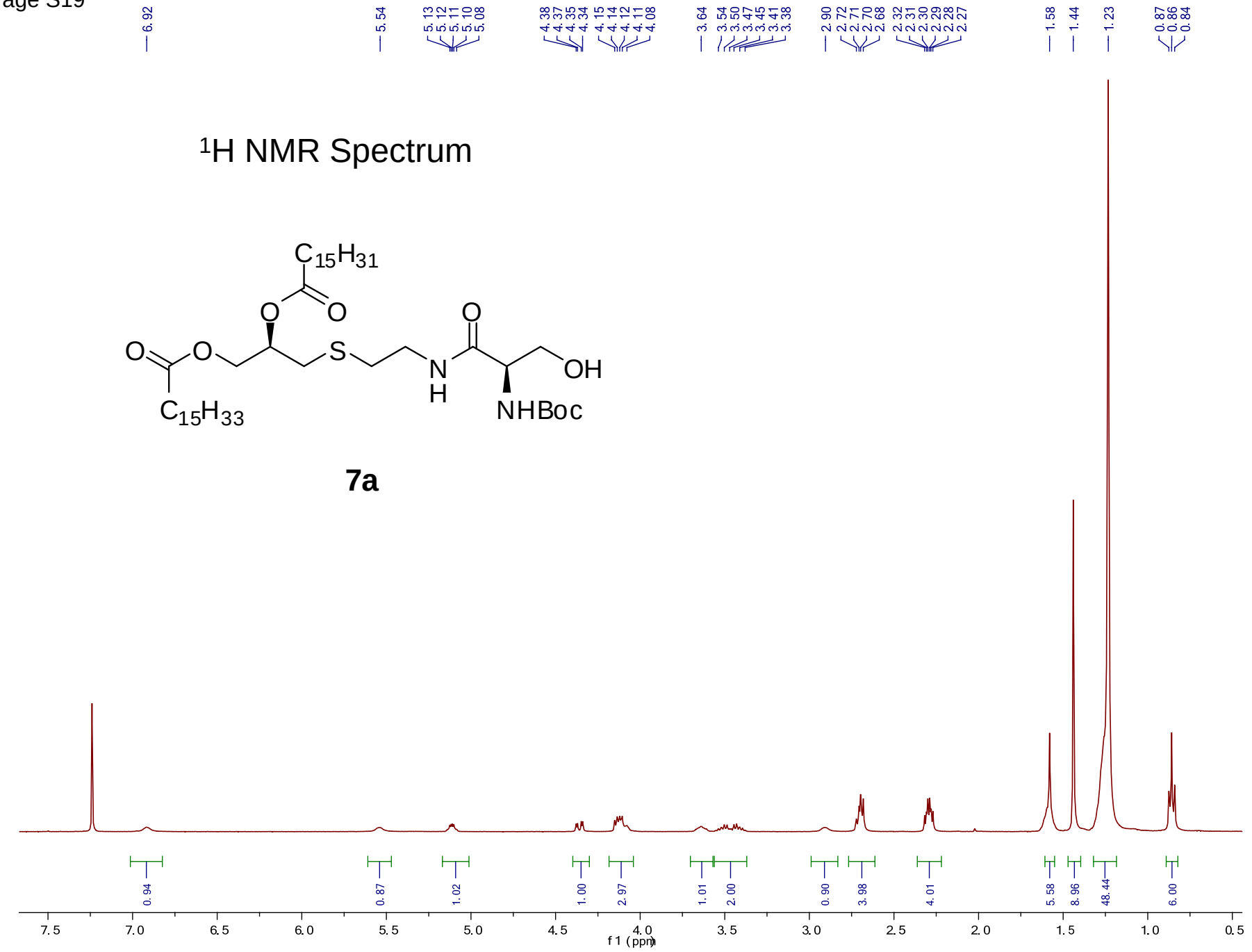


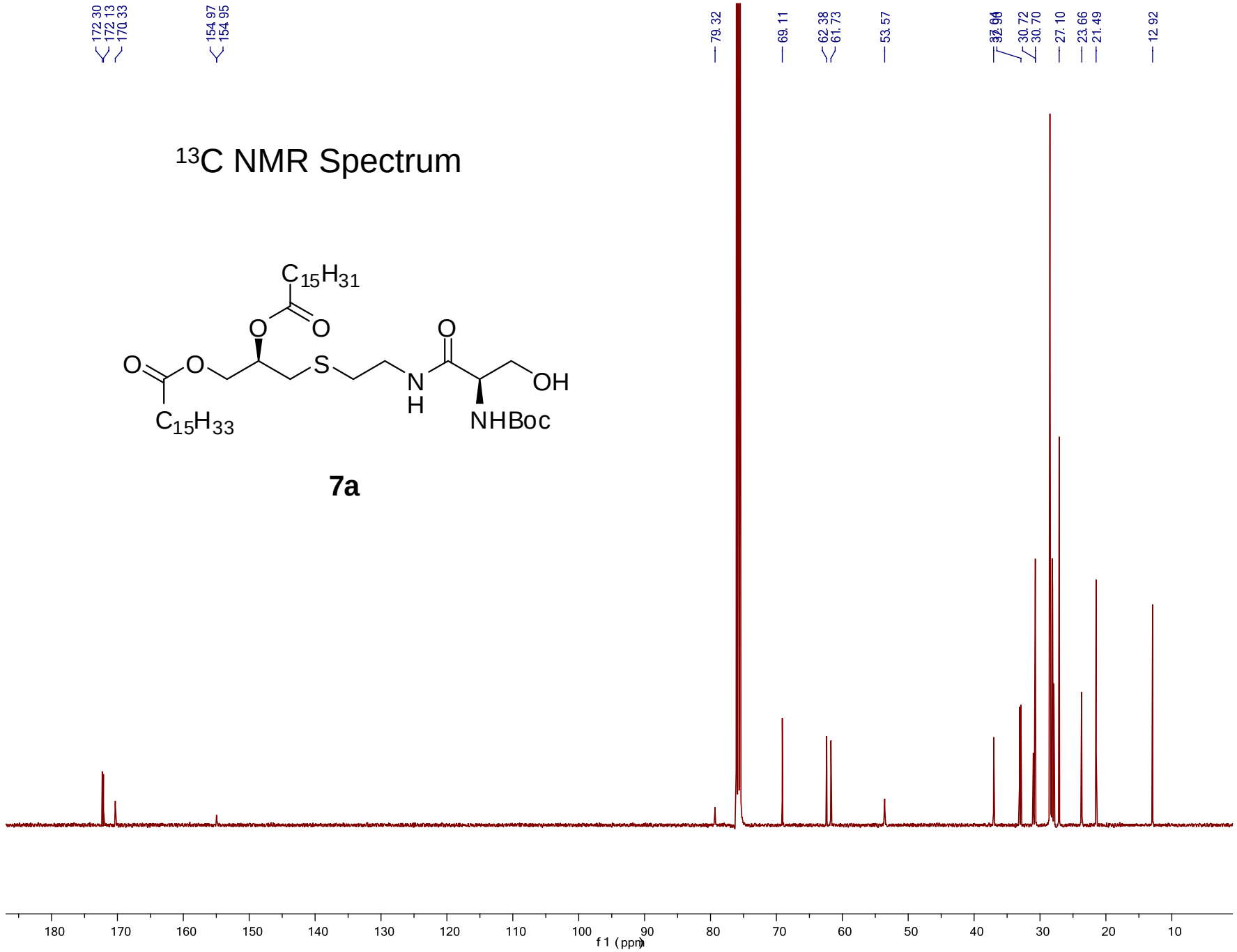
^{1}H NMR Spectrum

6b



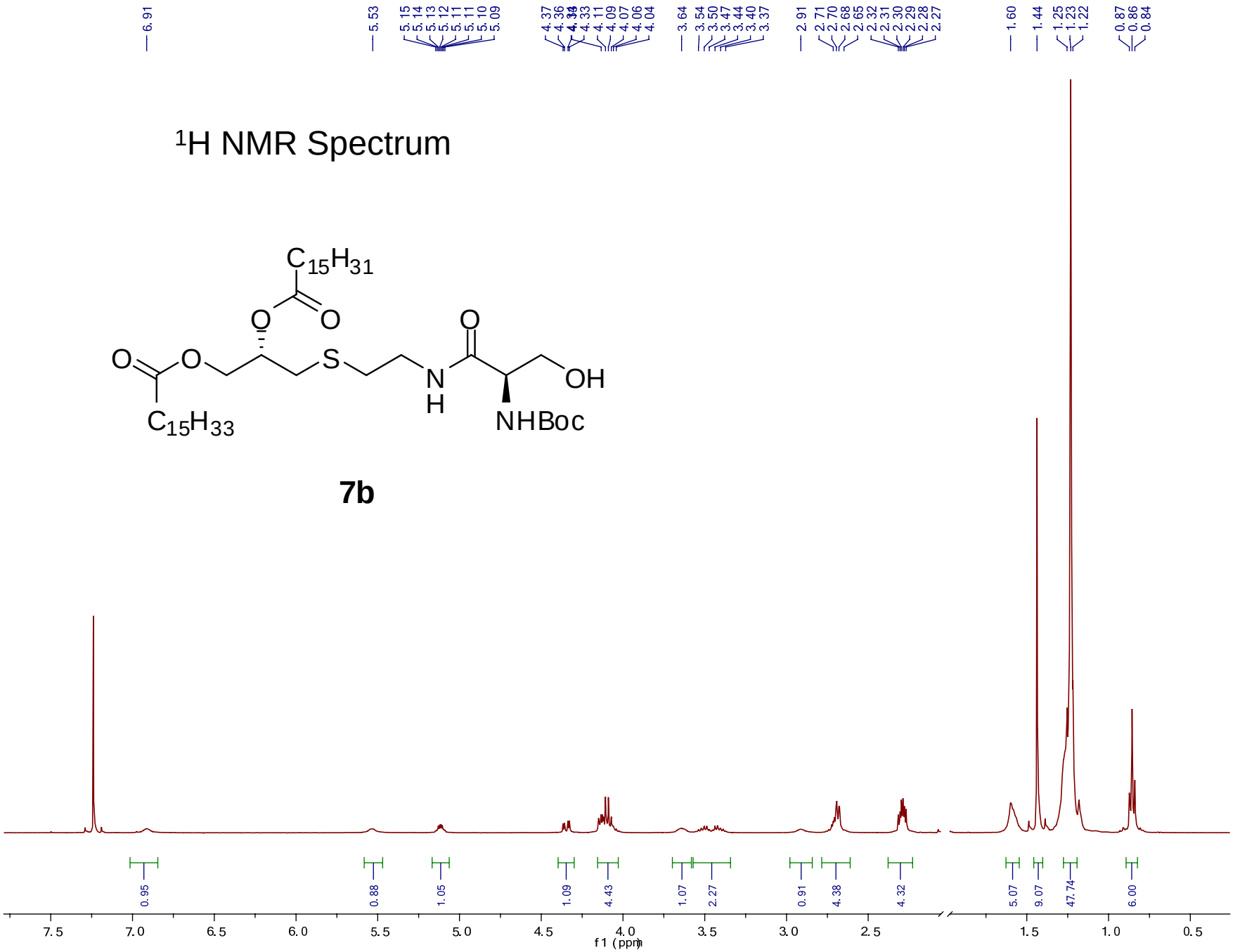

TOF Spectrum
TOF
Profile Spectrum at 9.09 min (scan 1)
Baseline = 1.37519300051467
Abundance Min = 0
Abundance Max = 2421436
628.50714
629.47851
630.47325
631.47355
600.44
Abundance
m/z
2.5M
2.0M
1.5M
1.0M
0.5M
0.0
500
1000
1500
2000
2500
3000
$C_{15}H_{31}$
$C_{15}H_{33}$
$NH_2 \bullet CF_3COOH$
6a R
6b S

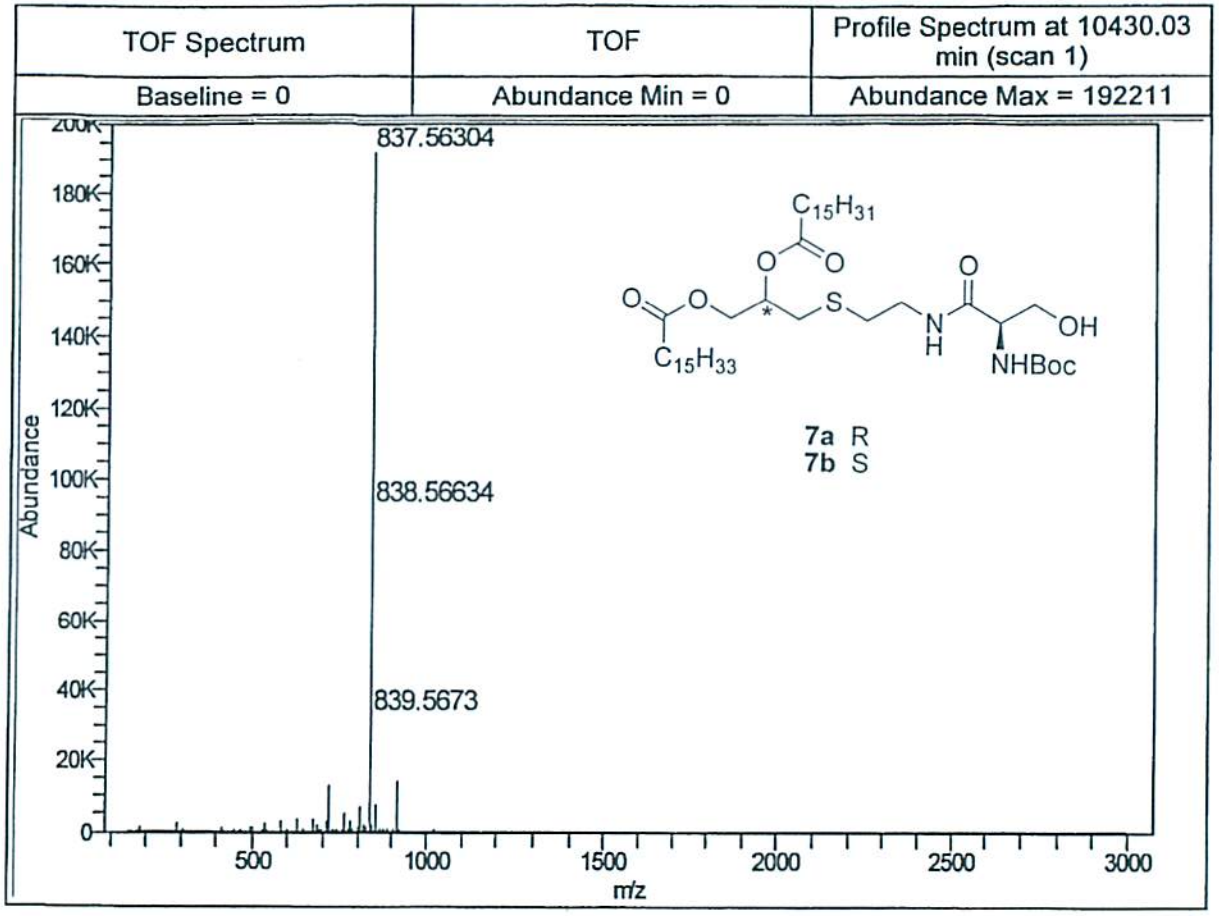

6.92
5.54
5.13
5.12
5.11
5.10
5.08
4.38
4.37
4.35
4.34
4.15
4.14
4.12
4.11
4.08
3.64
3.54
3.50
3.47
3.45
3.41
3.38
2.90
2.72
2.71
2.70
2.68
2.32
2.31
2.30
2.29
2.28
2.27
1.58
1.44
1.23
0.87
0.86
0.84
1H NMR Spectrum
C15H31
O
O
O
O
O
S
N
H
O
OH
C15H33
NHBoc
7a
0.94
0.87
1.02
1.00
2.97
1.01
2.00
0.90
3.98
4.01
5.58
8.96
48.44
6.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


172.30
172.13
170.33
154.97
154.95
79.32
69.11
62.38
61.73
53.57
32.04
30.72
30.70
27.10
23.66
21.49
12.92
13C NMR Spectrum
C15H31
O
O
O
O
S
N
H
O
OH
NHBoc
C15H33
7a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

^{1}H NMR Spectrum

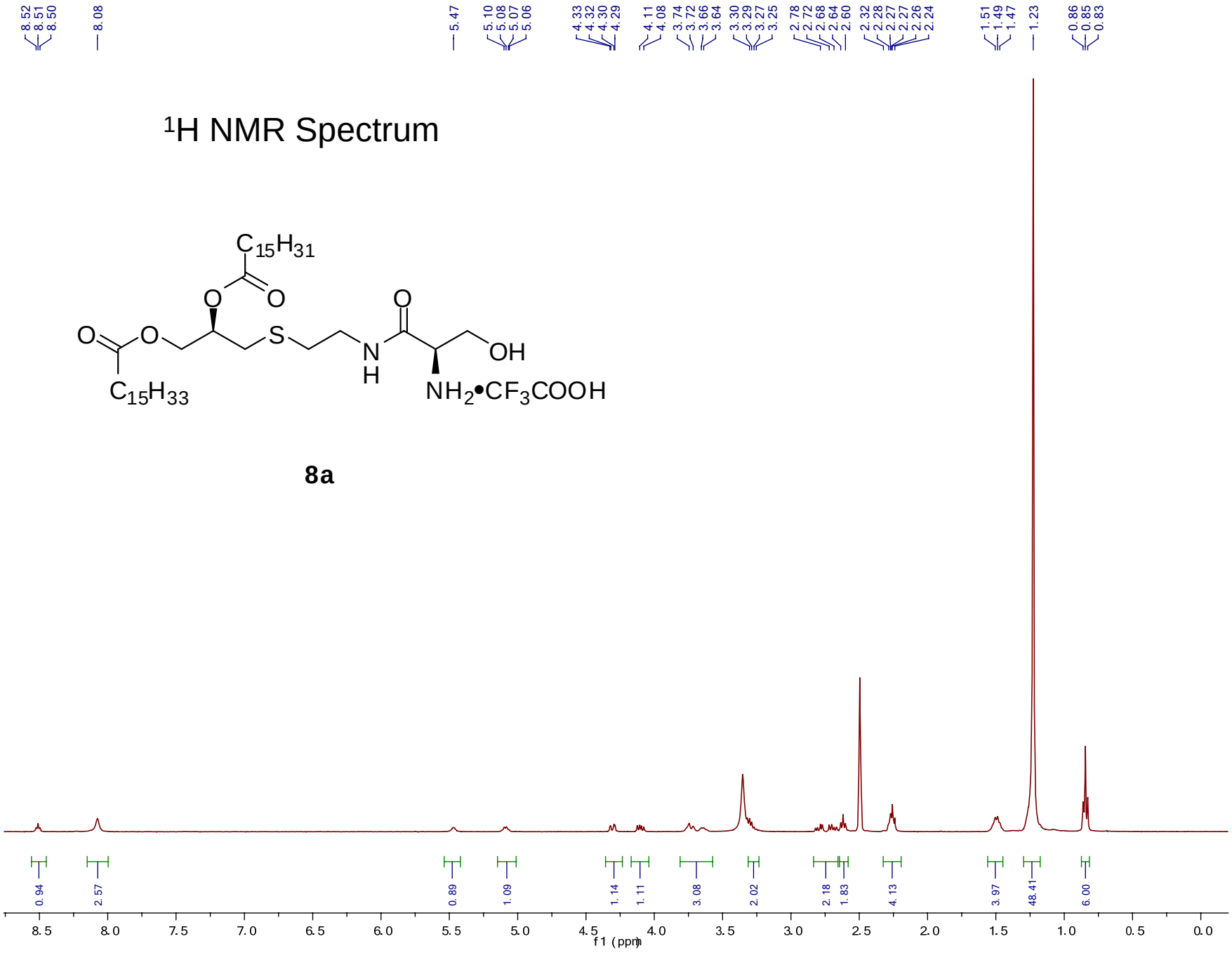
7b

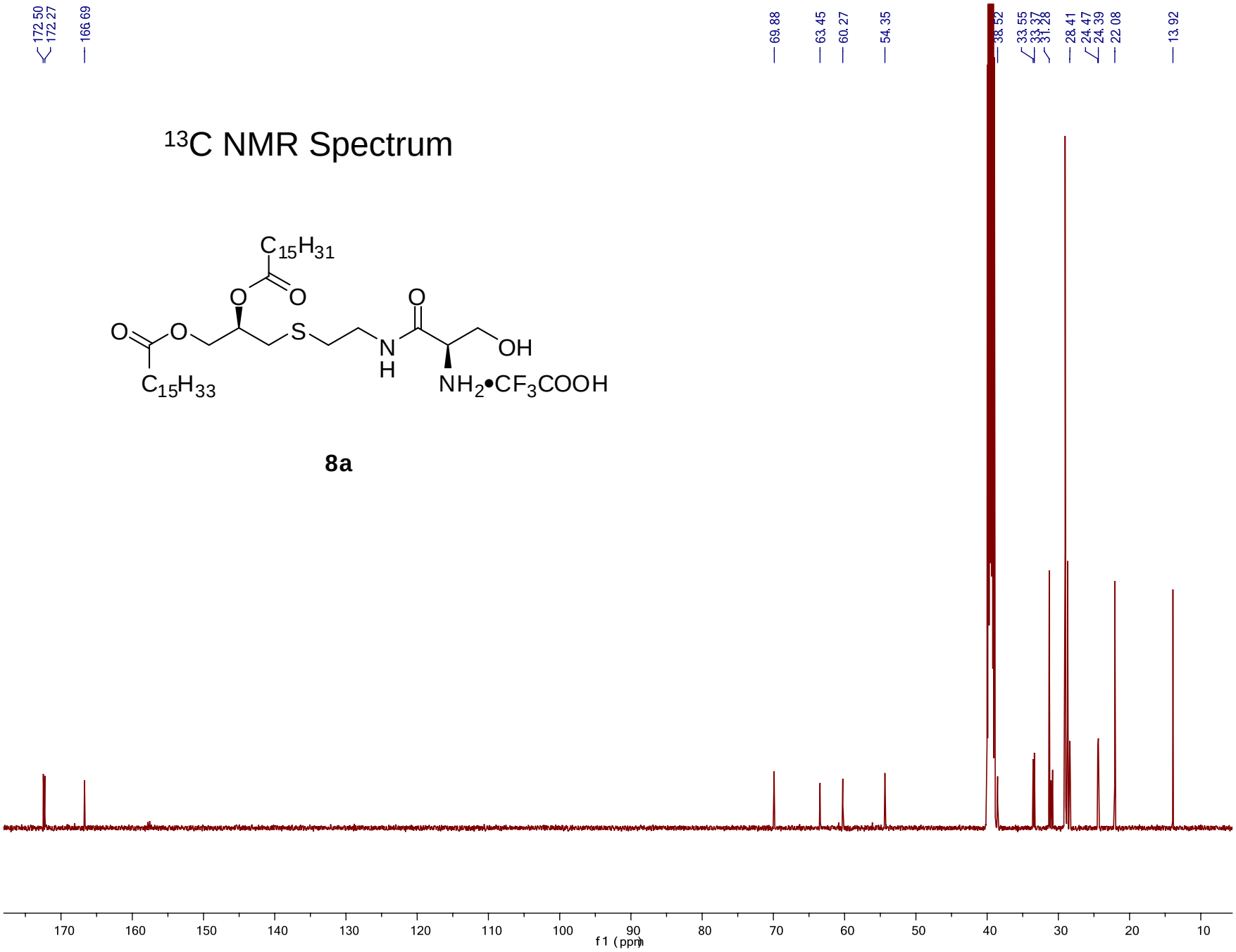



TOF Spectrum
TOF
Profile Spectrum at 10430.03 min (scan 1)
Baseline = 0
Abundance Min = 0
Abundance Max = 192211
837.56304
838.56634
839.5673
Abundance
m/z
200K
180K
160K
140K
120K
100K
80K
60K
40K
20K
0
500
1000
1500
2000
2500
3000
C15H31
C15H33
NHBoc
OH
7a R
7b S

^{1}H NMR Spectrum

8a



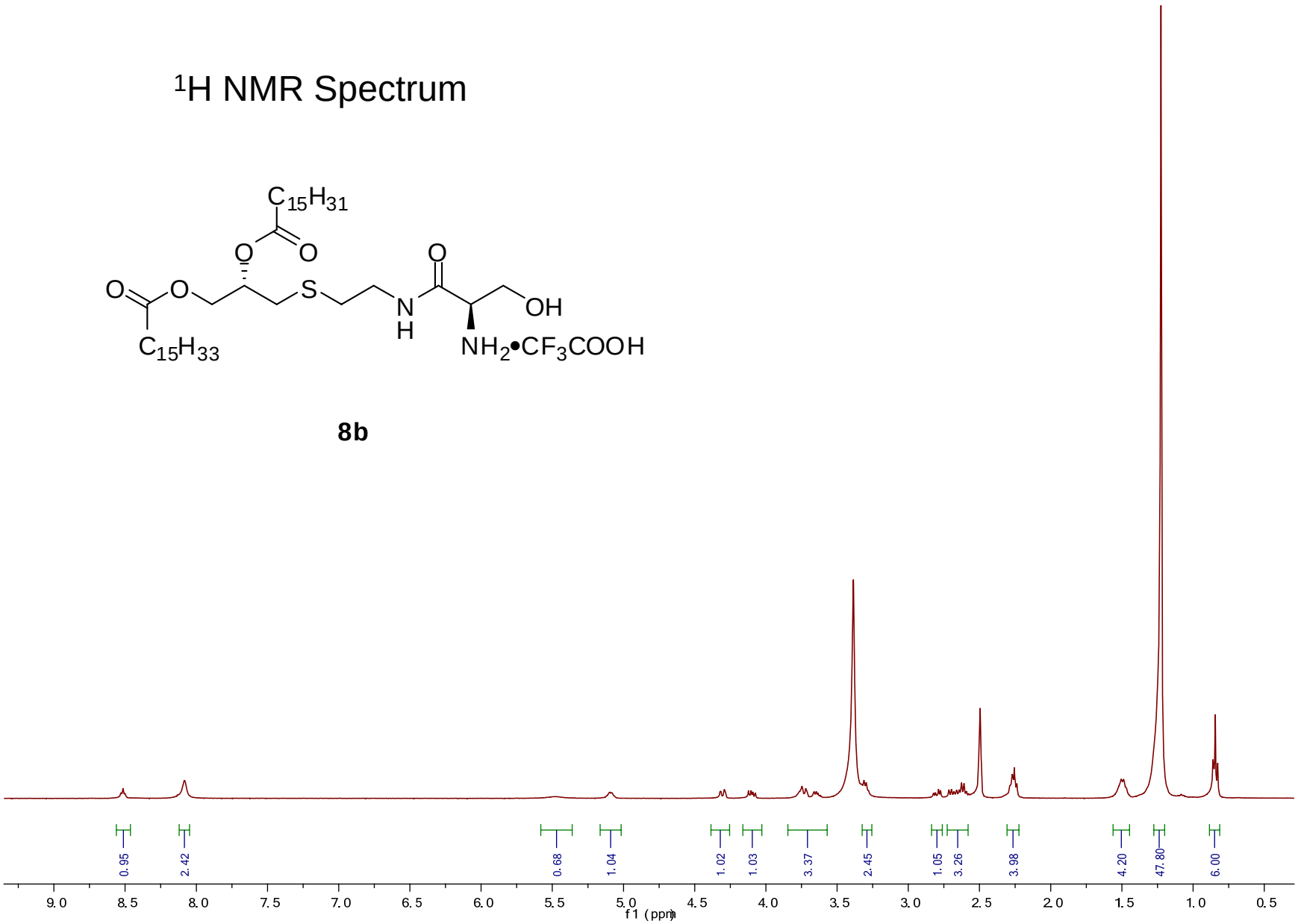


^{13}C NMR Spectrum

8a

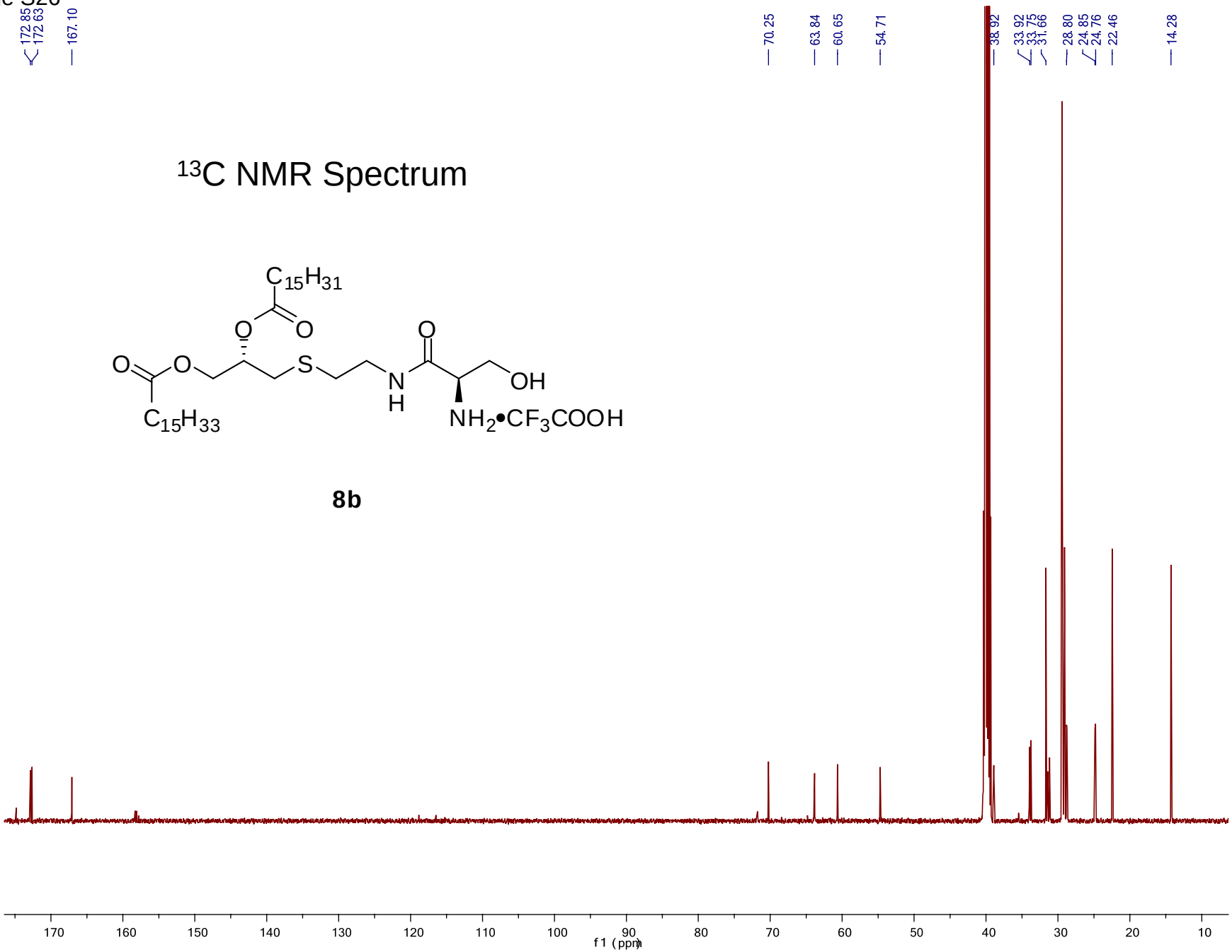
^{1}H NMR Spectrum

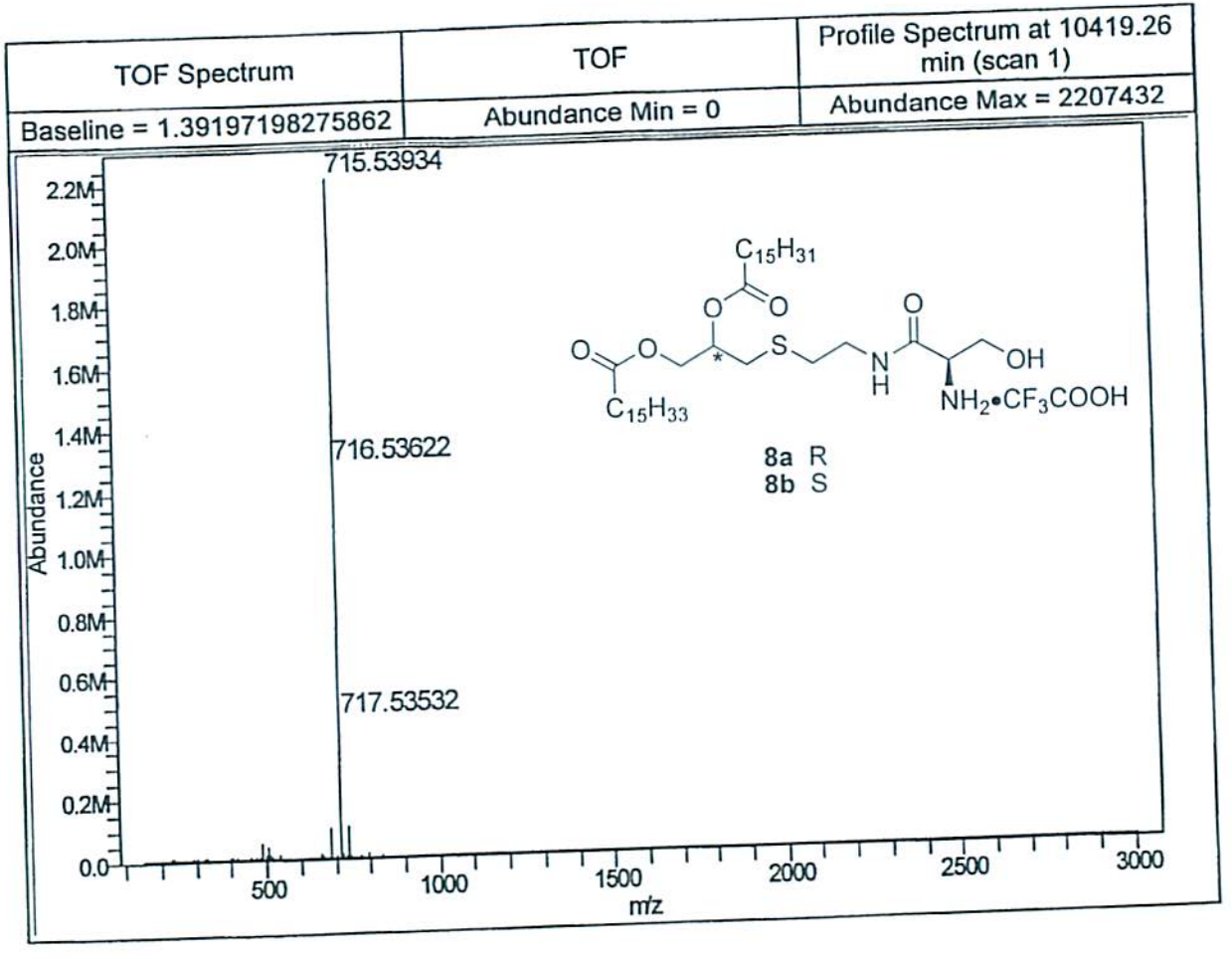
8b



^{13}C NMR Spectrum

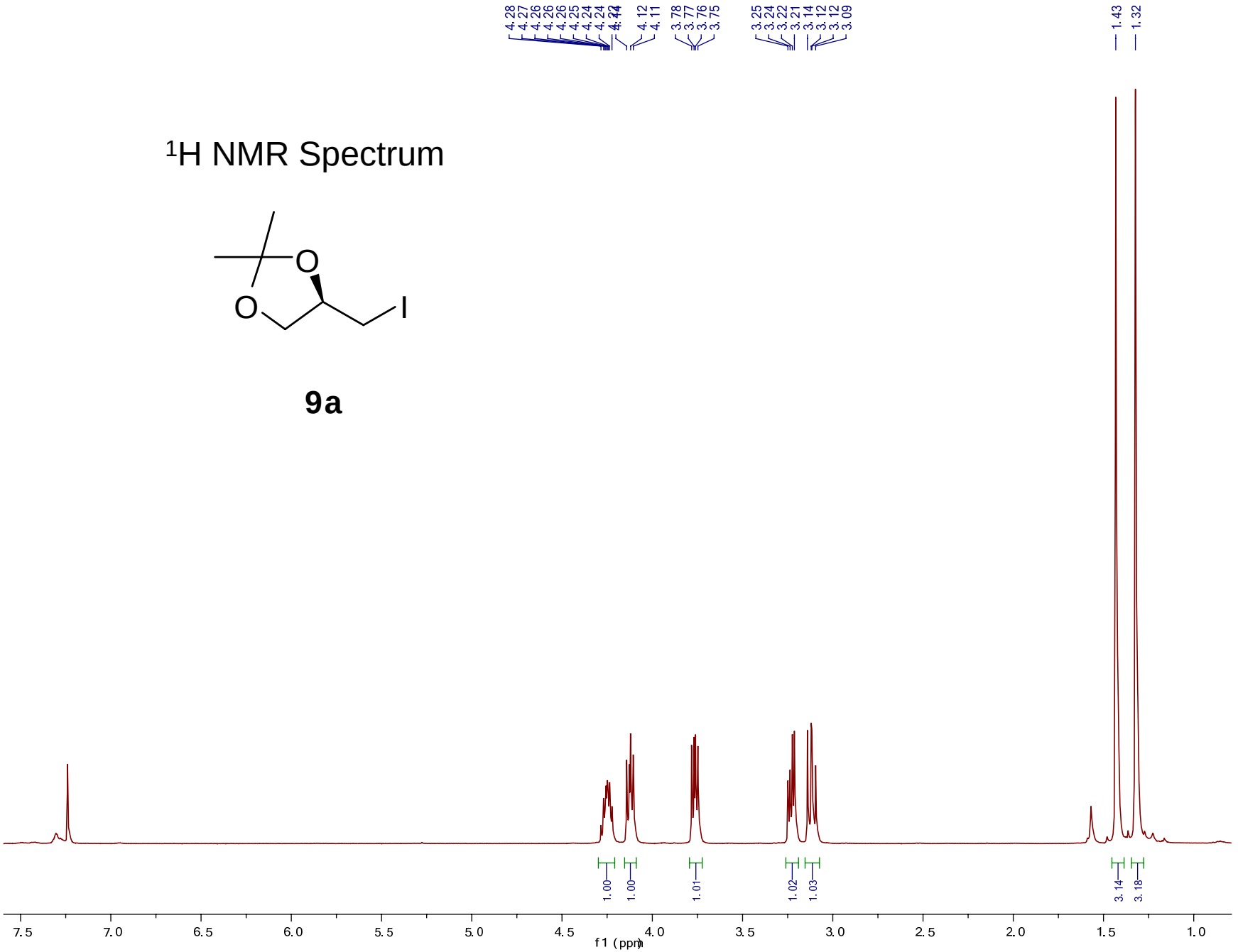
8b

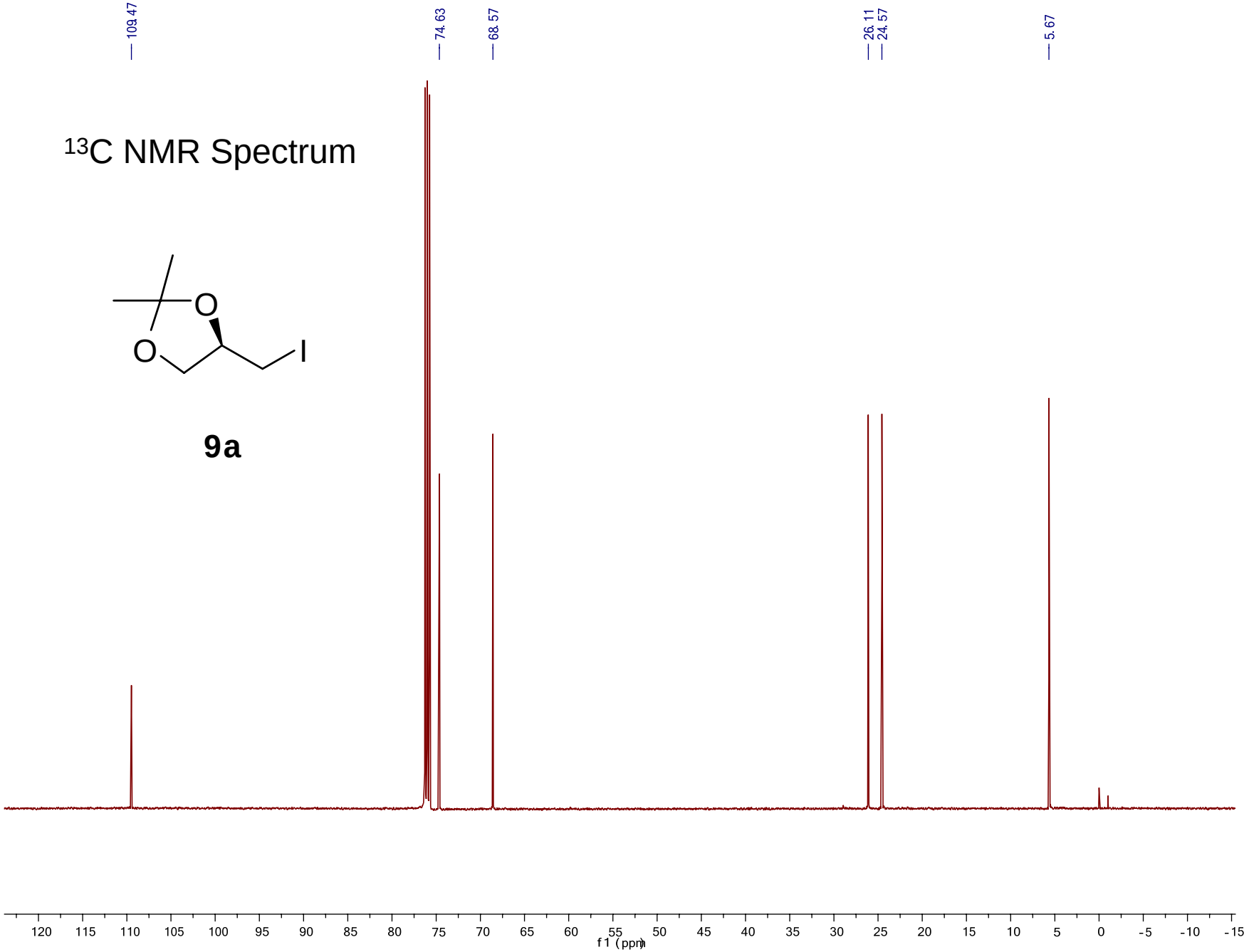



TOF Spectrum
TOF
Profile Spectrum at 10419.26 min (scan 1)
Baseline = 1.39197198275862
Abundance Min = 0
Abundance Max = 2207432
715.53934
716.53622
717.53532
Abundance
m/z
2.2M
2.0M
1.8M
1.6M
1.4M
1.2M
1.0M
0.8M
0.6M
0.4M
0.2M
0.0
500
1000
1500
2000
2500
3000
C15H31
C15H33
NH2•CF3COOH
8a R
8b S

^{1}H NMR Spectrum

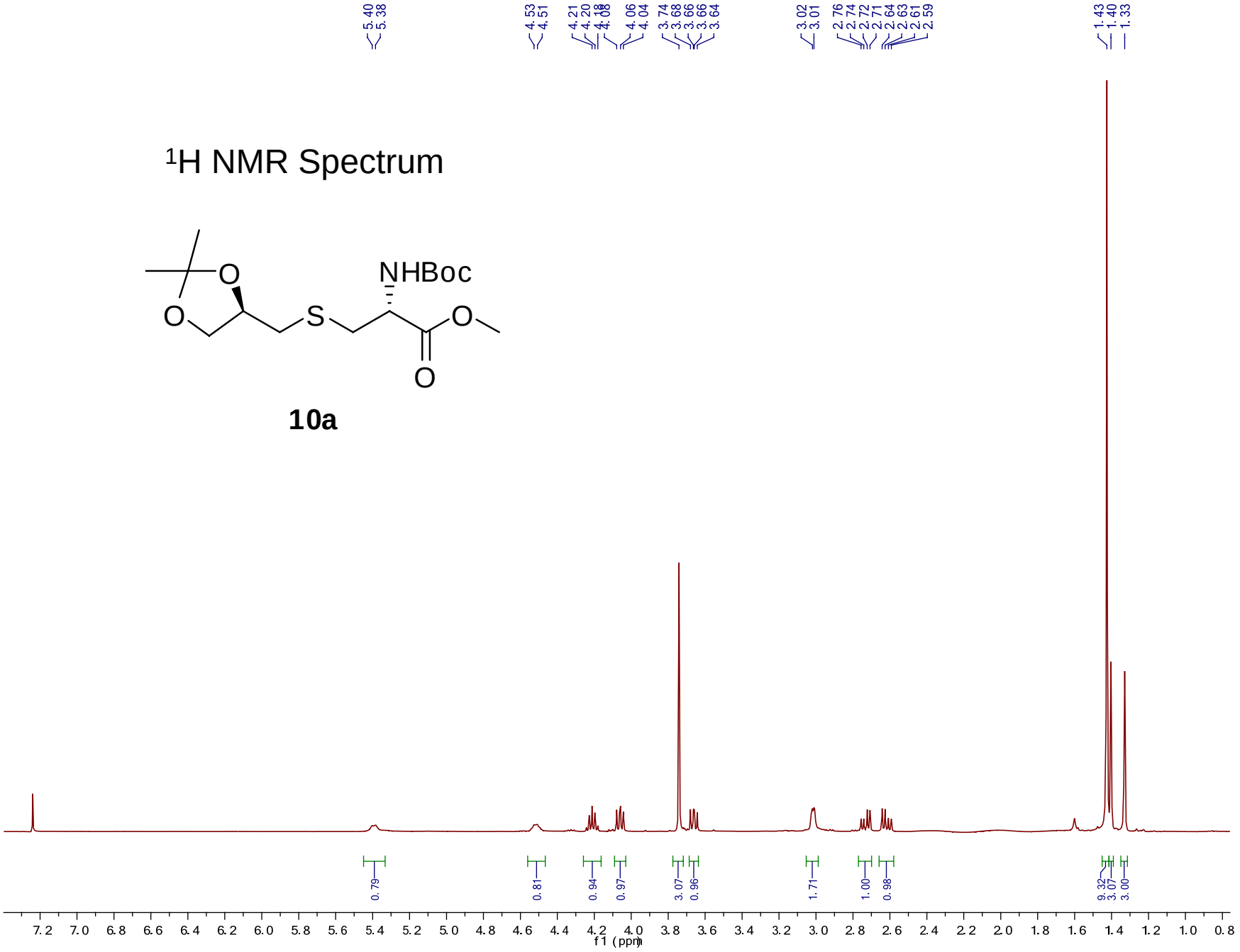
9a




109.47
74.63
68.57
26.11
24.57
5.67
13C NMR Spectrum
O
O
I
9a
120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15
f1 (ppm)

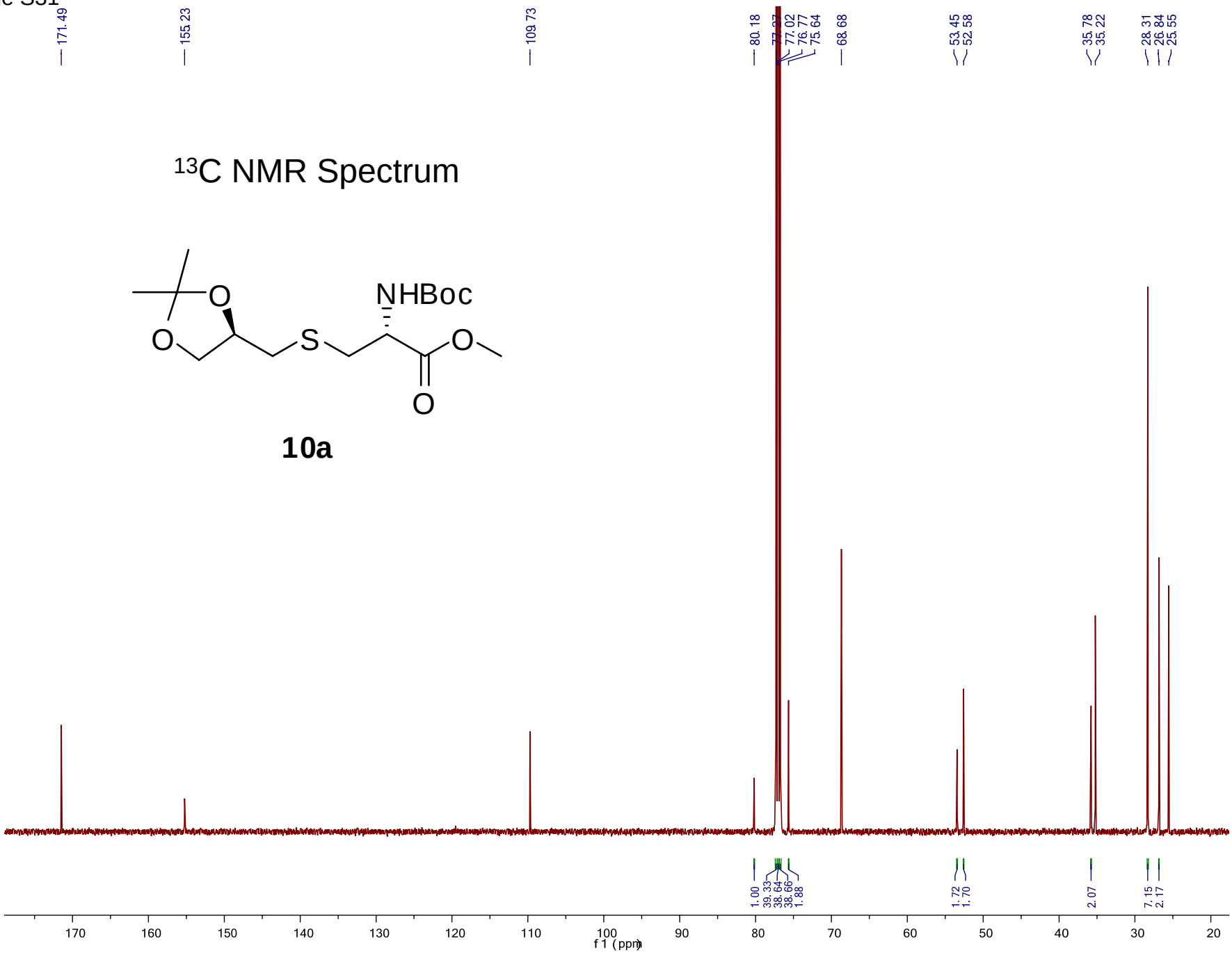
^{1}H NMR Spectrum

10a



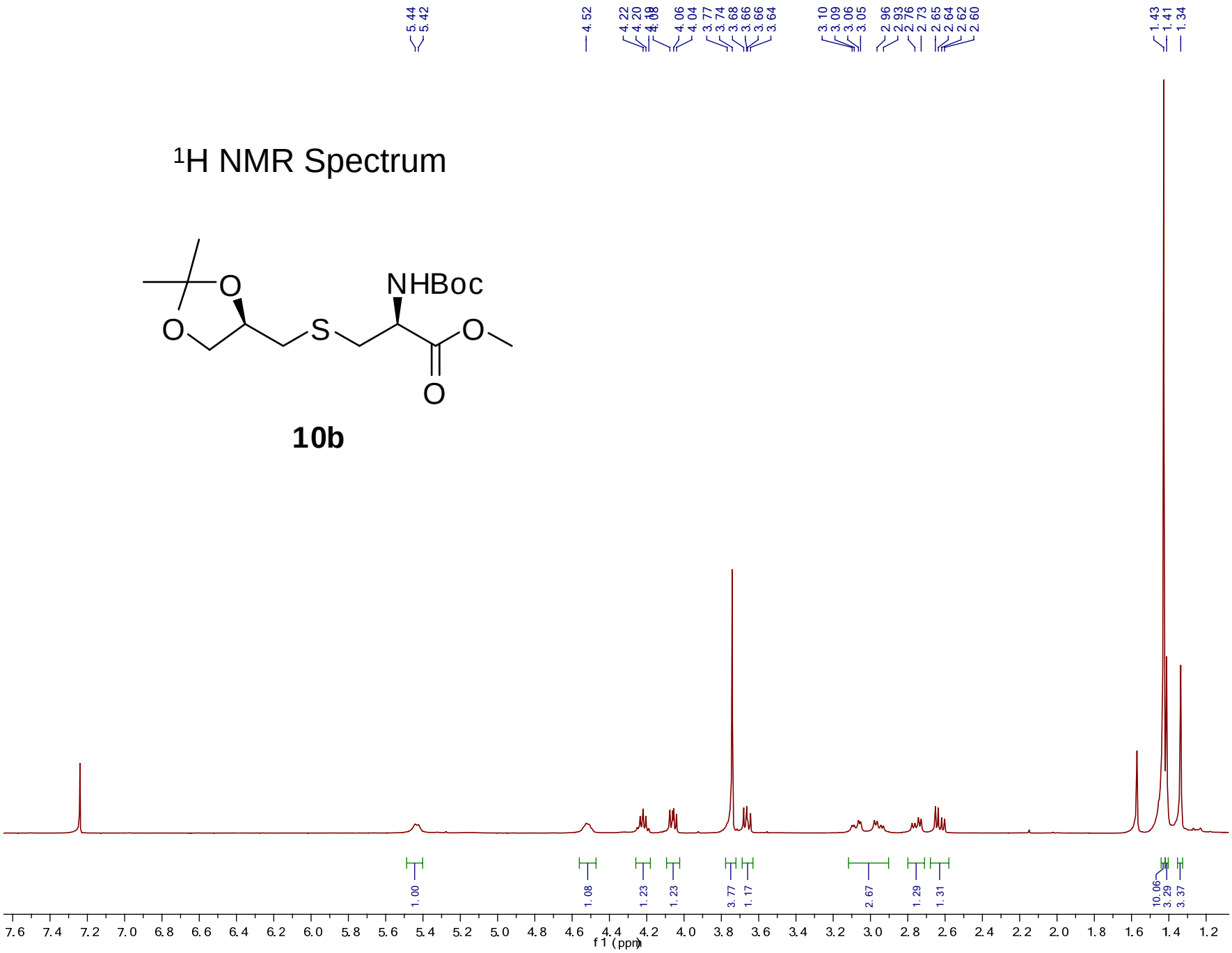
^{13}C NMR Spectrum

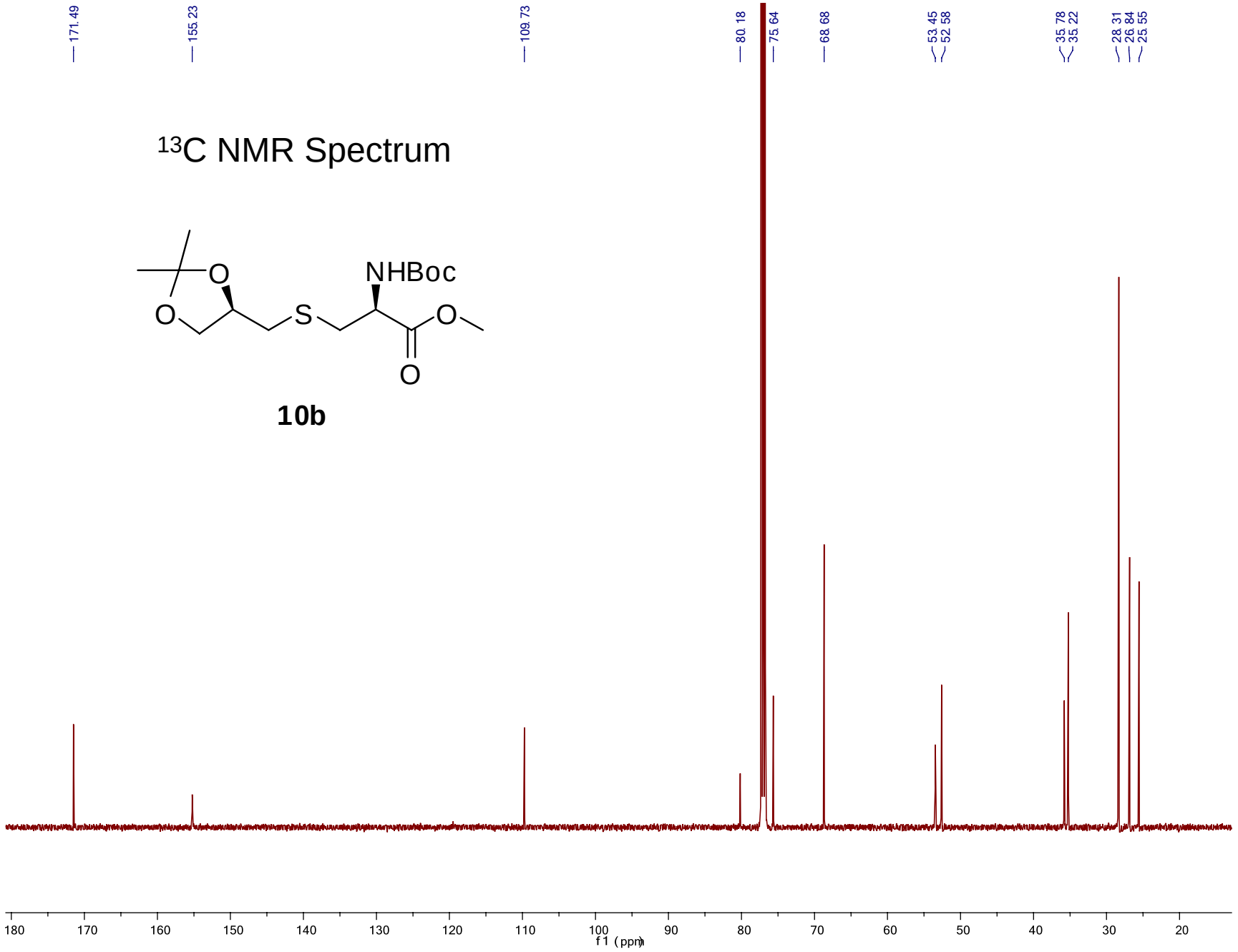
10a

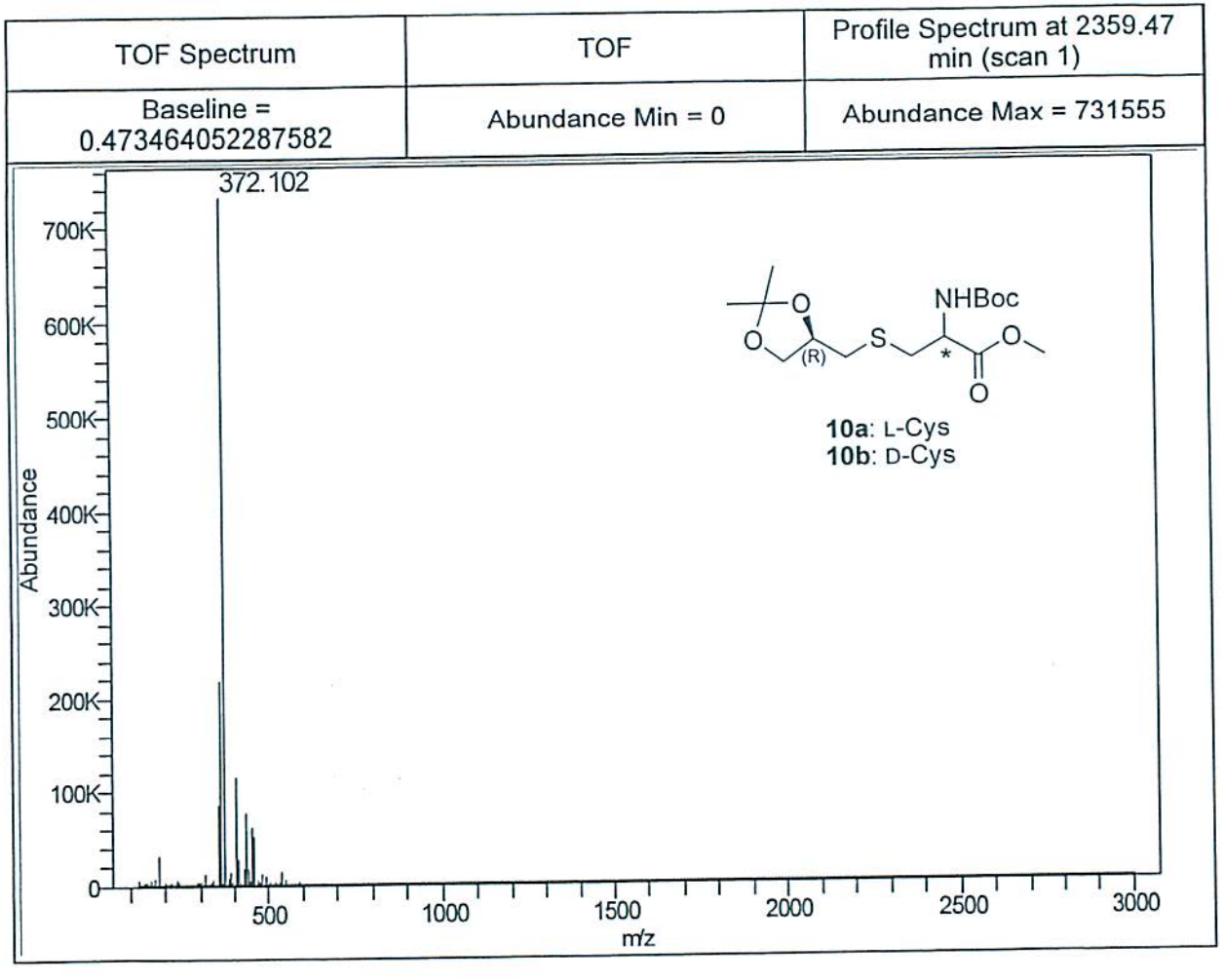


^{1}H NMR Spectrum

10b

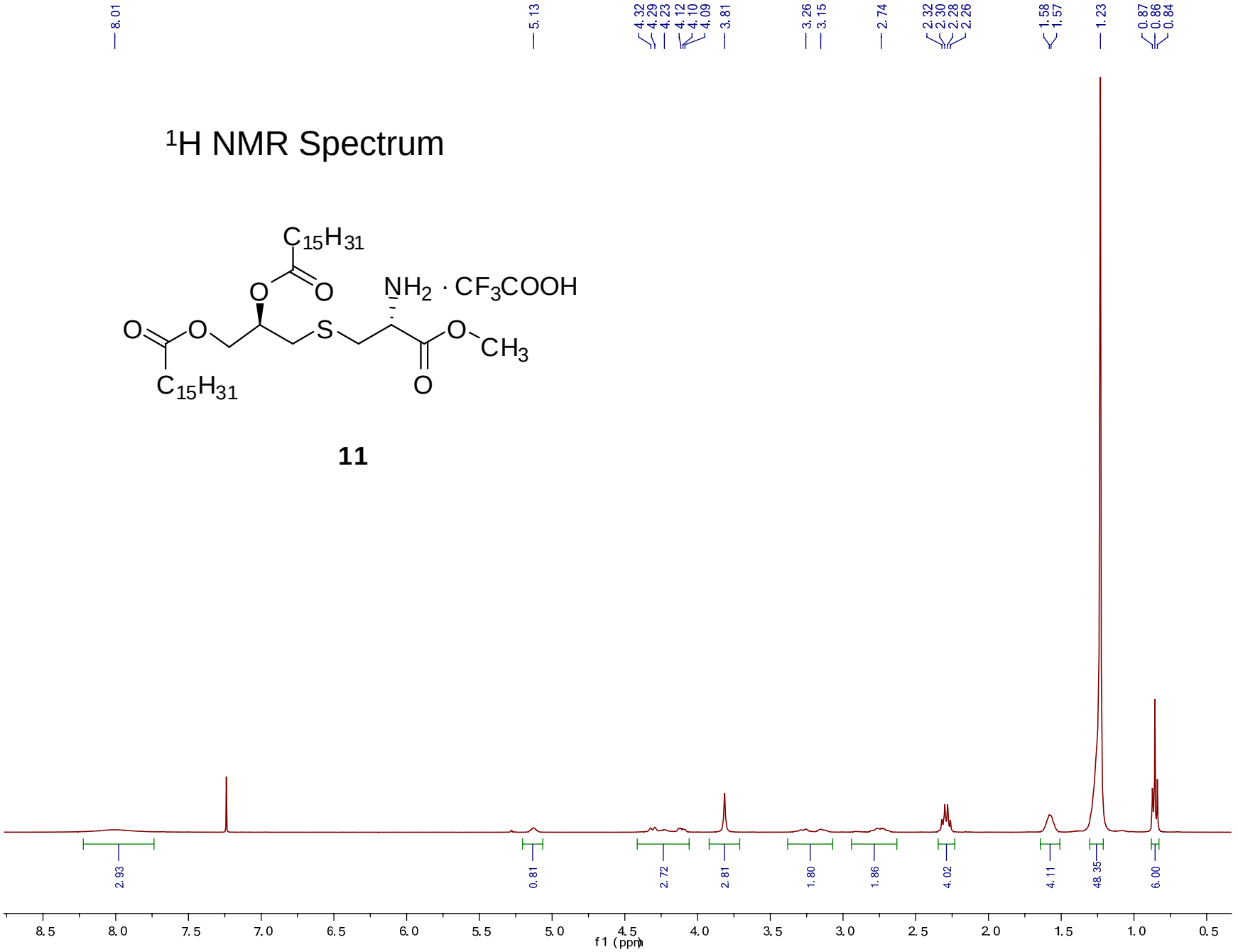


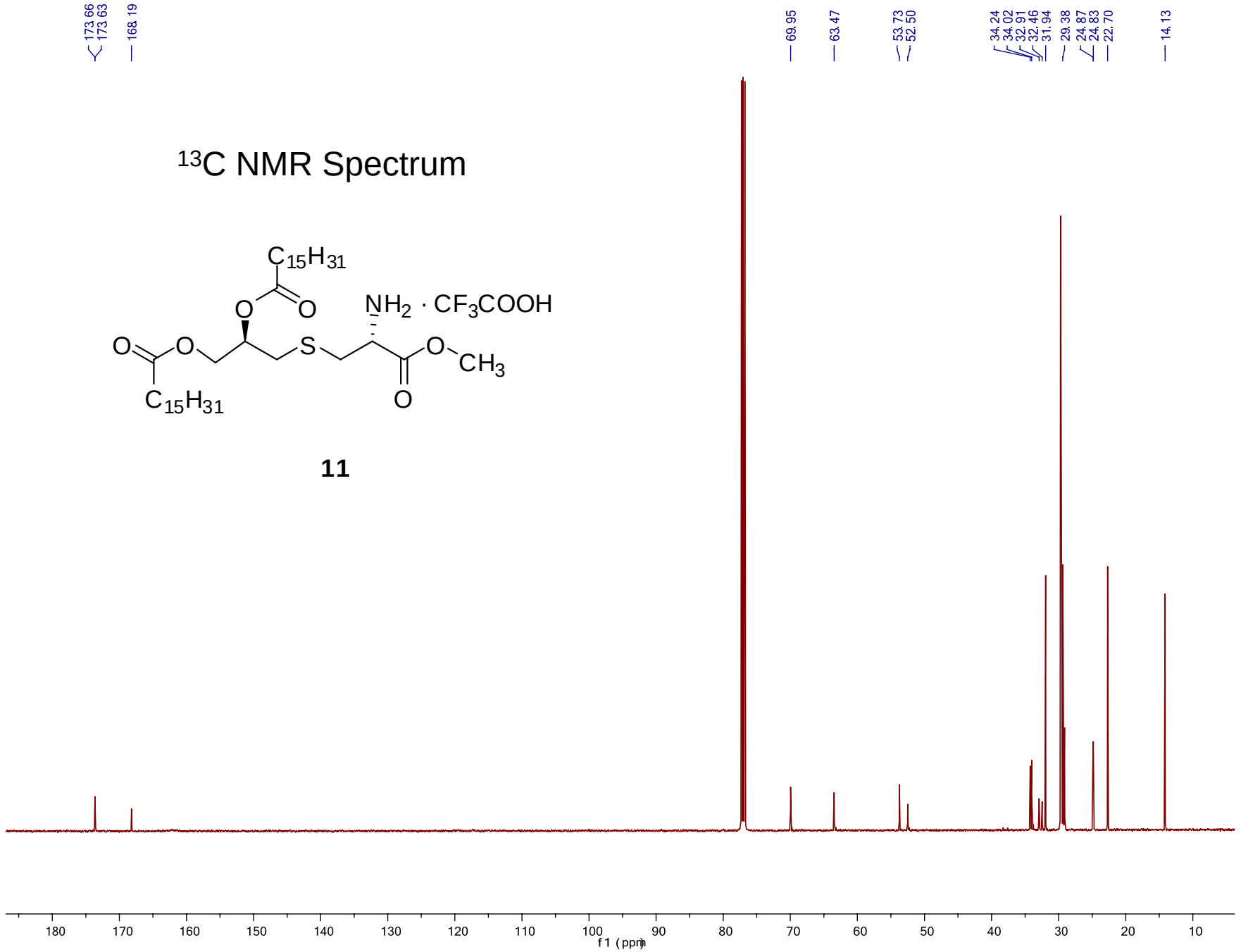

171.49
155.23
109.73
80.18
75.64
68.68
53.45
52.58
35.78
35.22
28.31
26.84
25.55
^{13}C NMR Spectrum
O
O
S
NHBoc
O
O
10b
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

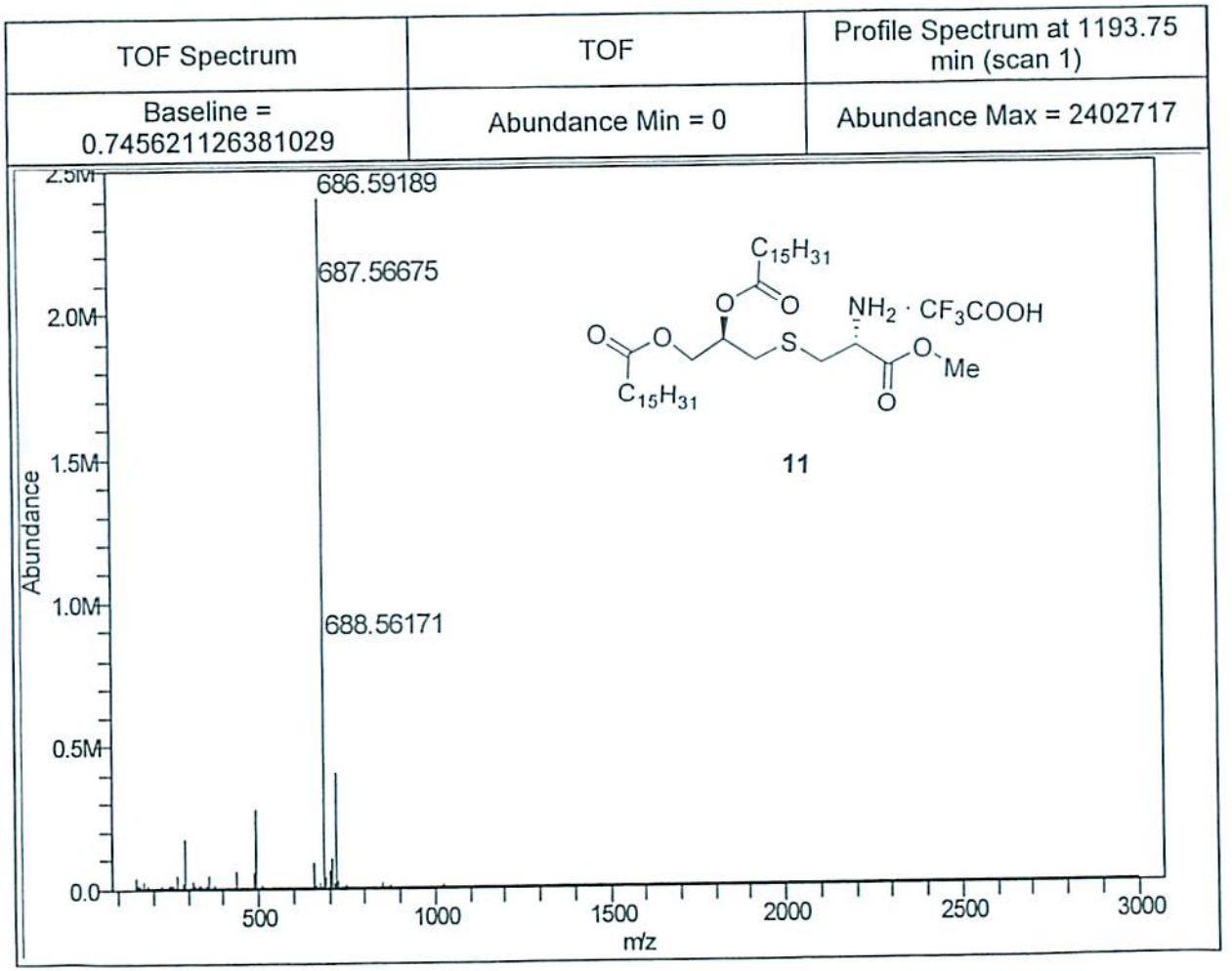

TOF Spectrum
TOF
Profile Spectrum at 2359.47 min (scan 1)
Baseline = 0.473464052287582
Abundance Min = 0
Abundance Max = 731555
372.102
Abundance
700K
600K
500K
400K
300K
200K
100K
0
500
1000
1500
2000
2500
3000
m/z
NHBoc
O
O
(R)
S
*
O
O
10a: L-Cys
10b: D-Cys

^{1}H NMR Spectrum

11

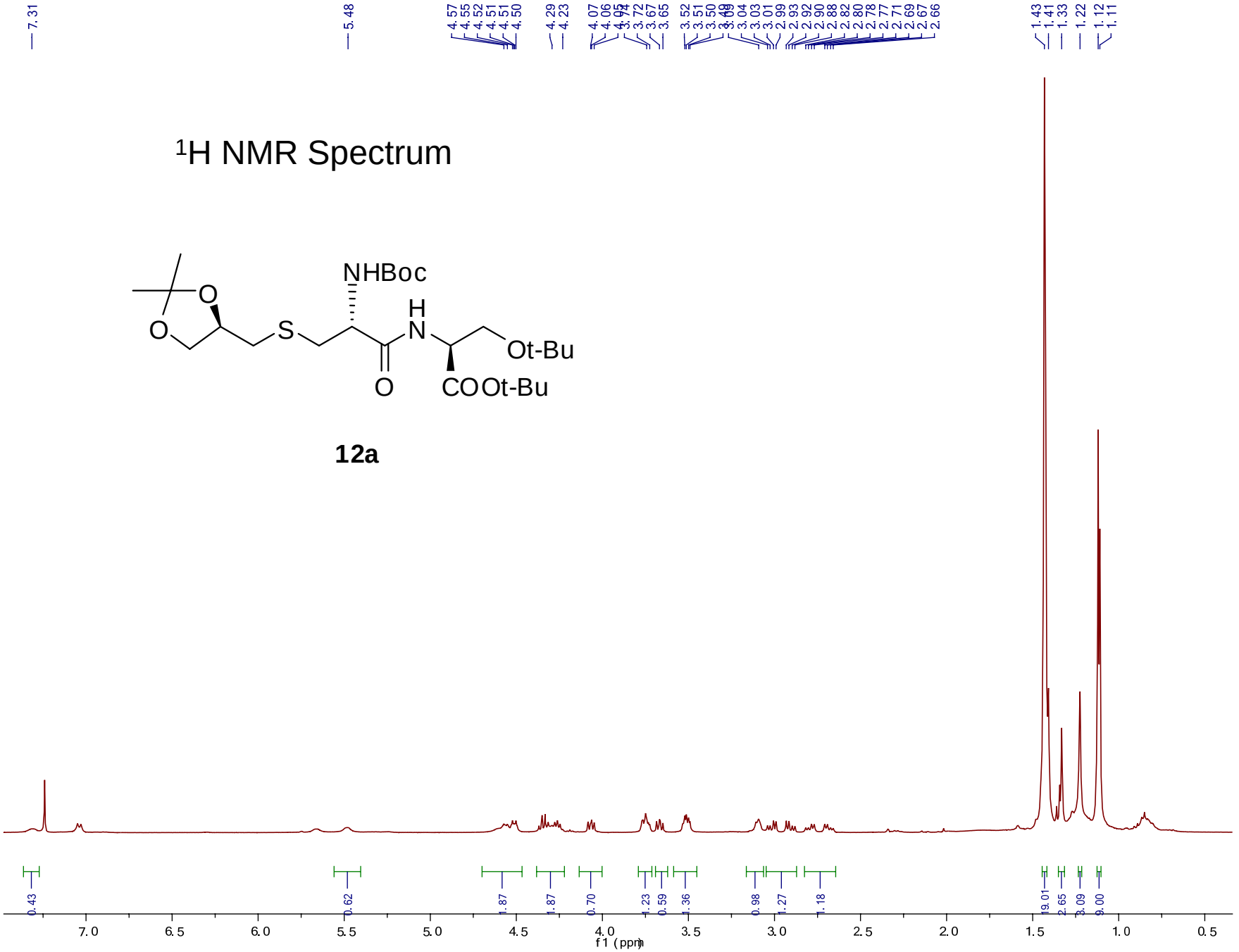


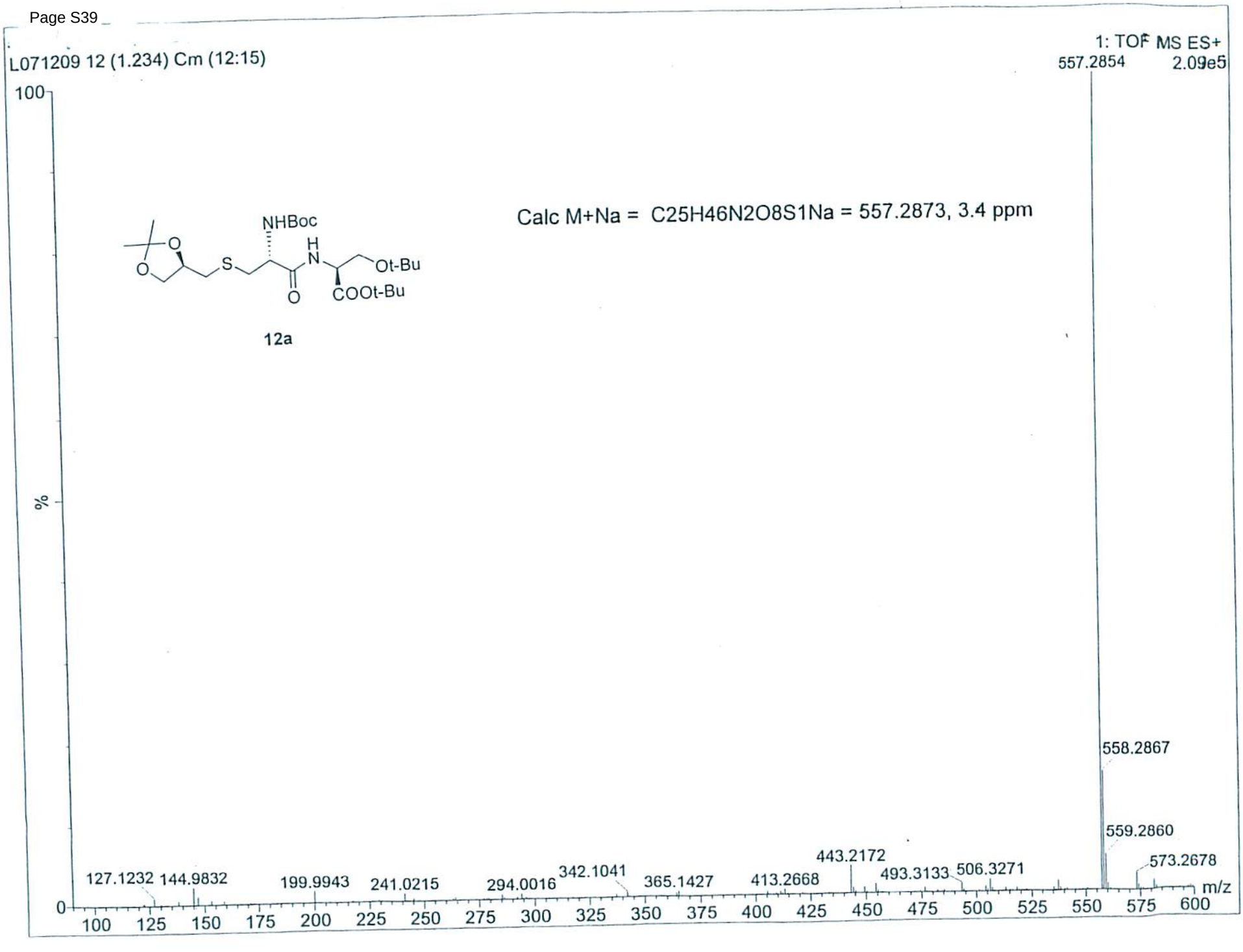

173.66
173.63
168.19
69.95
63.47
53.73
52.50
34.24
34.02
32.91
32.46
31.94
29.38
24.87
24.83
22.70
14.13
13C NMR Spectrum
C15H31
O
O
NH2 · CF3COOH
O
O
S
O
CH3
C15H31
O
11
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


TOF Spectrum
TOF
Profile Spectrum at 1193.75 min (scan 1)
Baseline = 0.745621126381029
Abundance Min = 0
Abundance Max = 2402717
686.59189
687.56675
688.56171
Abundance
m/z
2.5M
2.0M
1.5M
1.0M
0.5M
0.0
500
1000
1500
2000
2500
3000
$C_{15}H_{31}$
$NH_2 \cdot CF_3COOH$
Me
11

^{1}H NMR Spectrum

12a

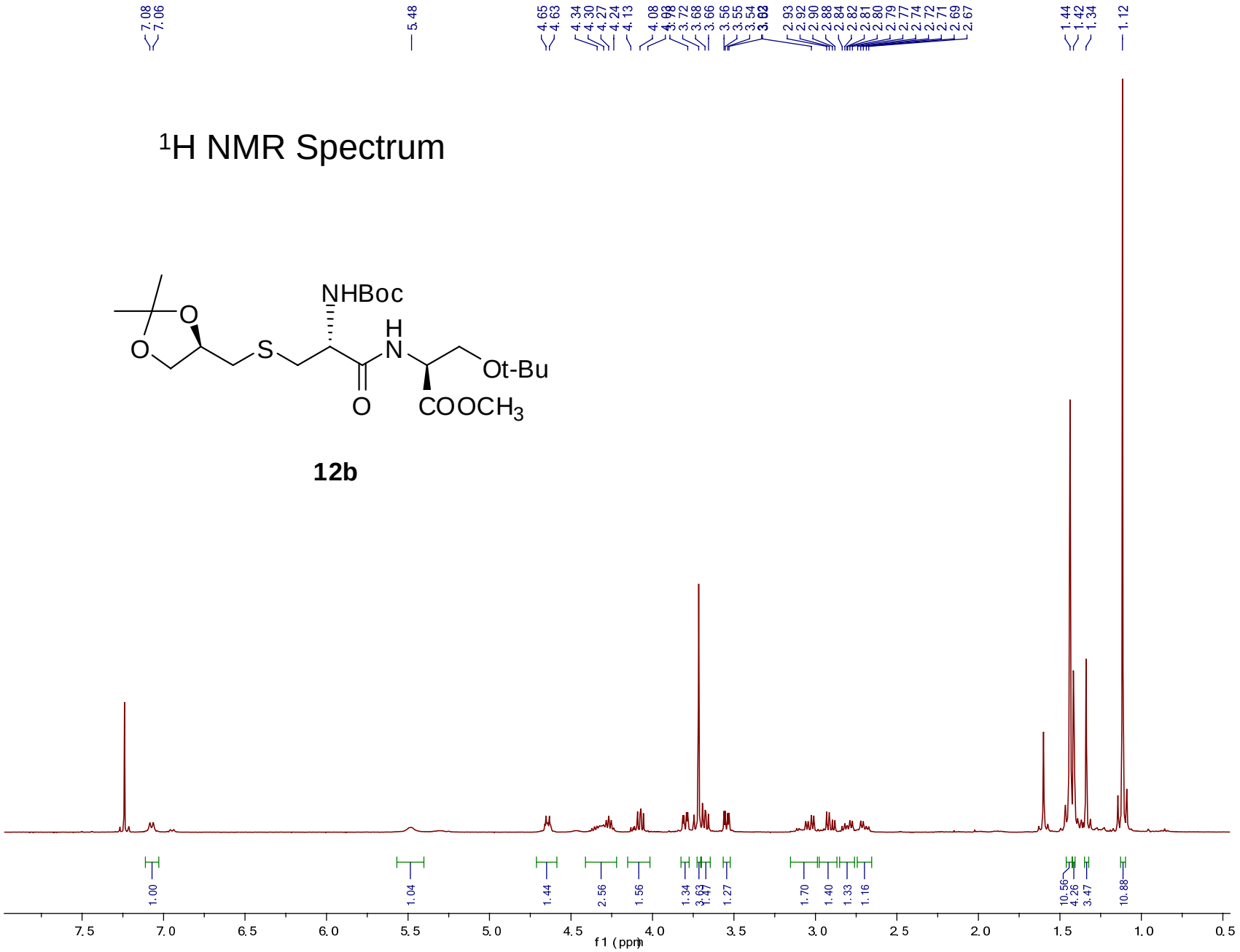



L071209 12 (1.234) Cm (12:15)
1: TOF MS ES+
557.2854
2.09e5
100
%
0
NHBoc
H
N
O
S
O
O
Ot-Bu
COOt-Bu
Calc M+Na = C25H46N2O8S1Na = 557.2873, 3.4 ppm
558.2867
559.2860
573.2678
443.2172
493.3133
506.3271
127.1232
144.9832
199.9943
241.0215
294.0016
342.1041
365.1427
413.2668
m/z
100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600

12a

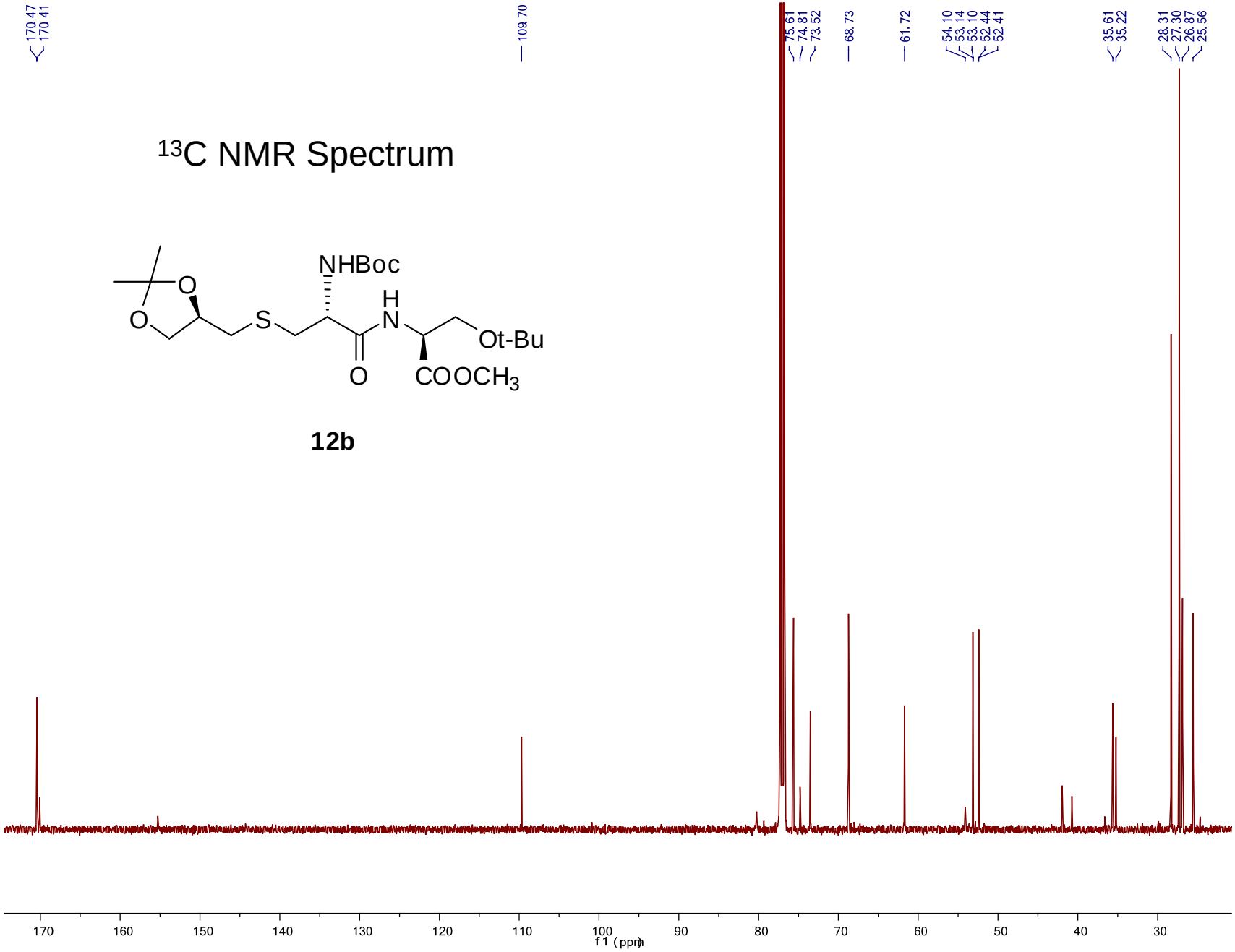
^{1}H NMR Spectrum

12b



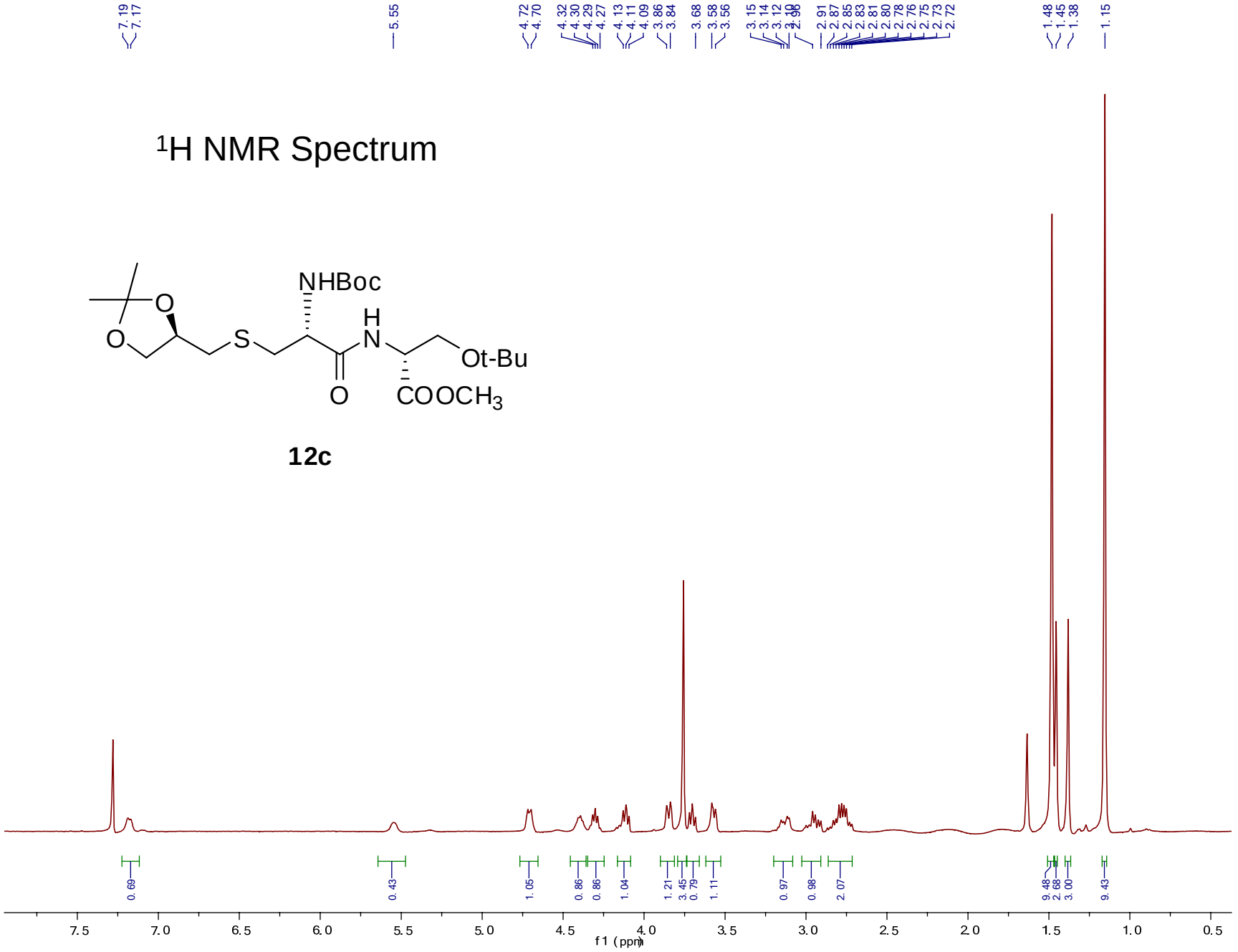
^{13}C NMR Spectrum

12b



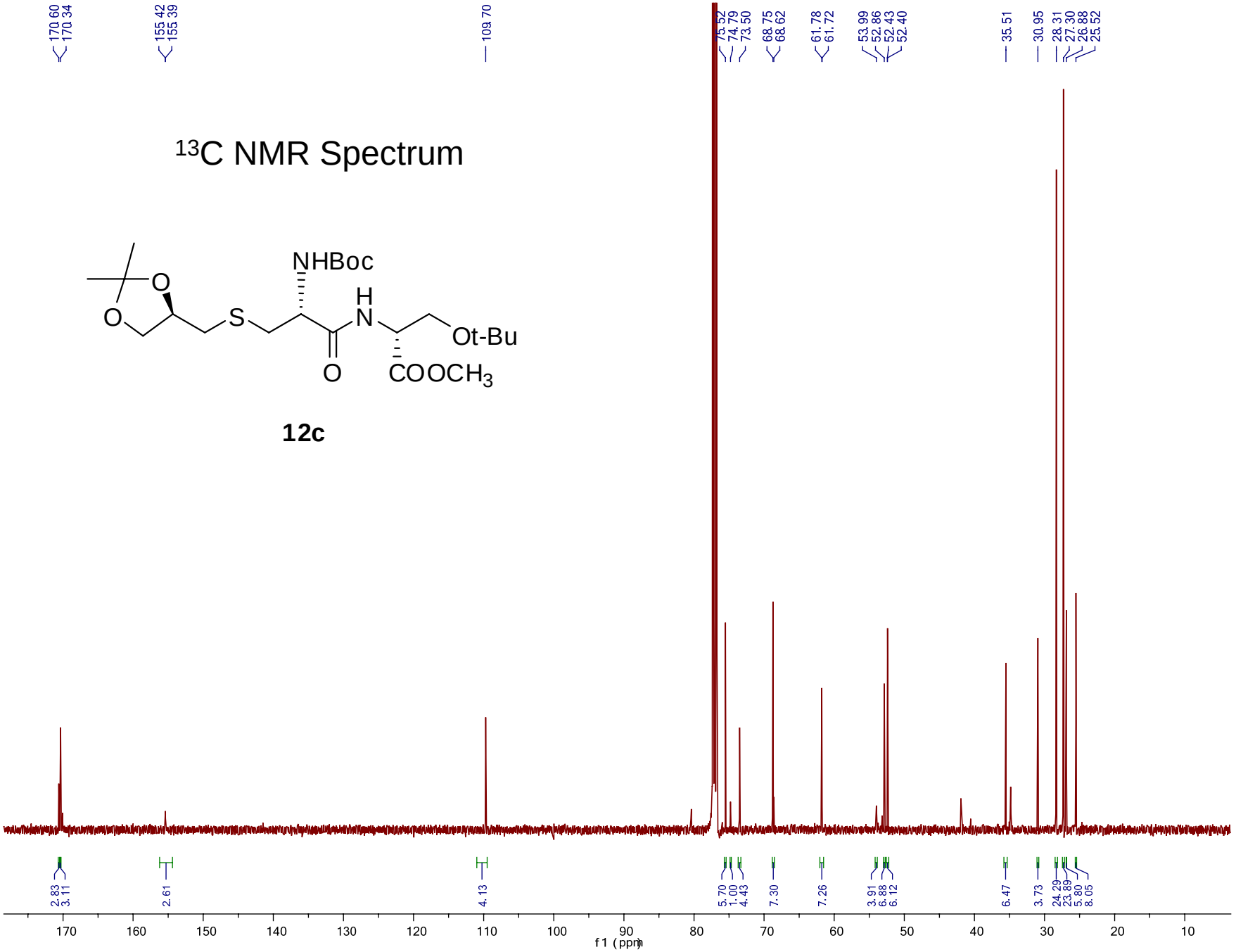
^{1}H NMR Spectrum

12c



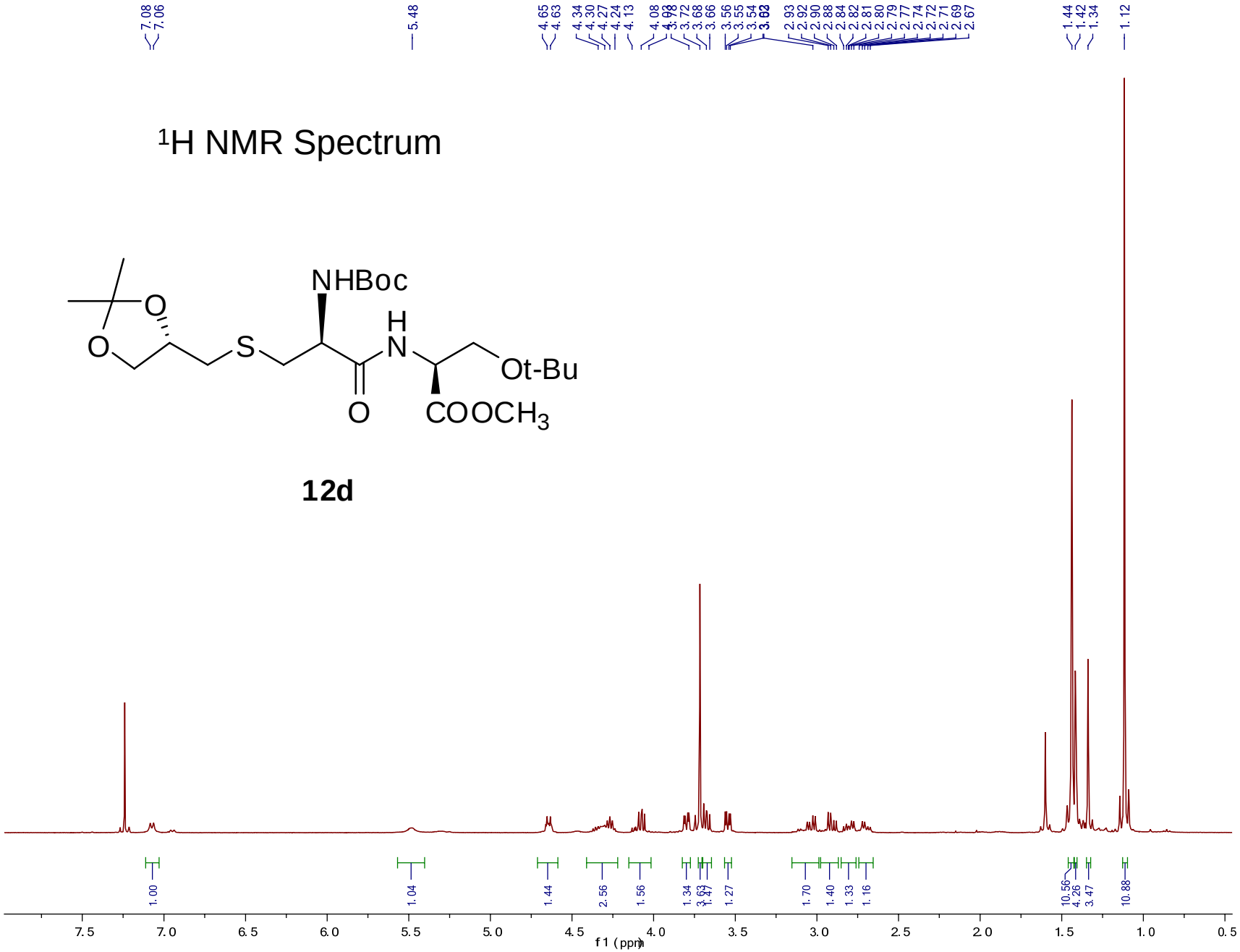
^{13}C NMR Spectrum

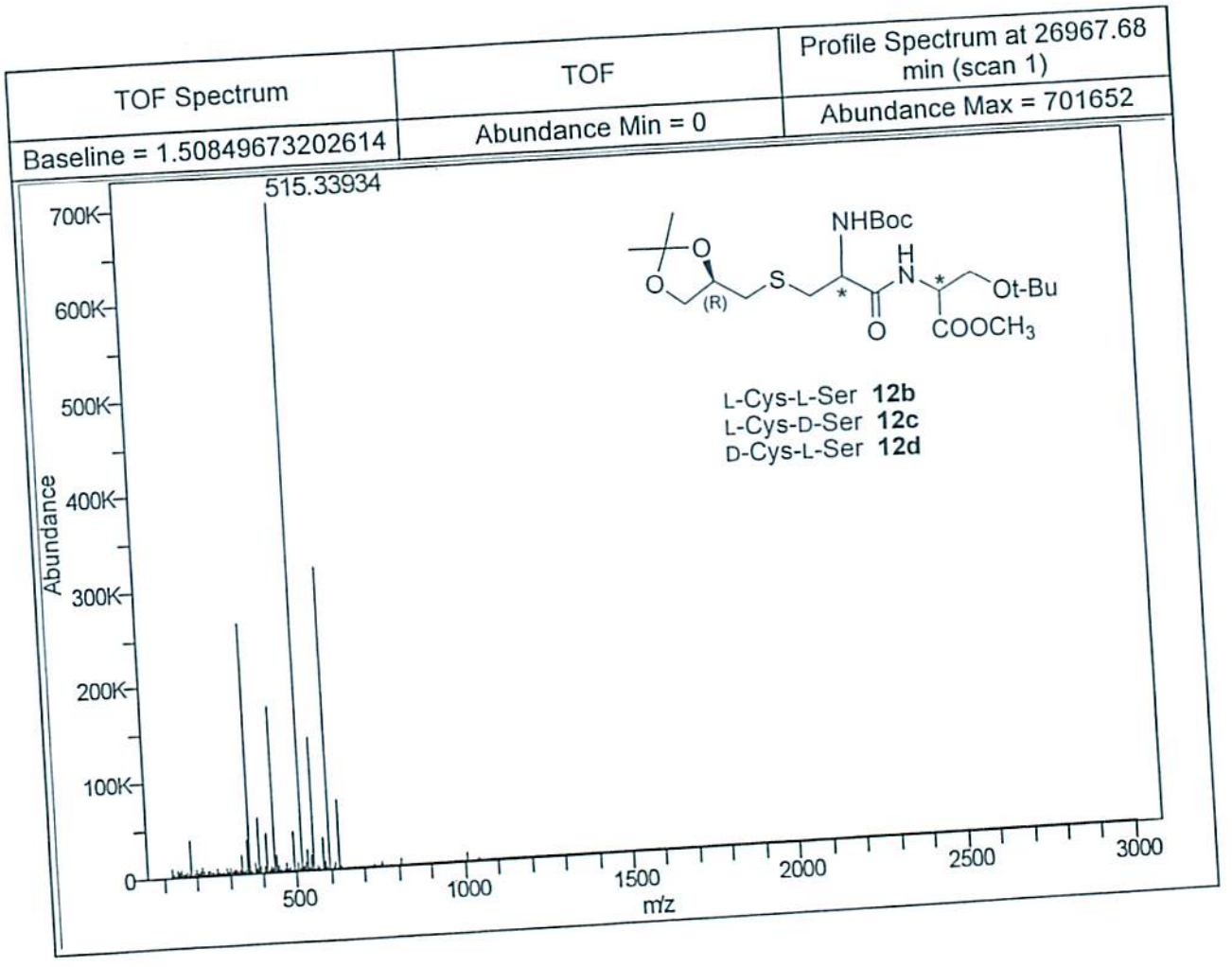
12c



^{1}H NMR Spectrum

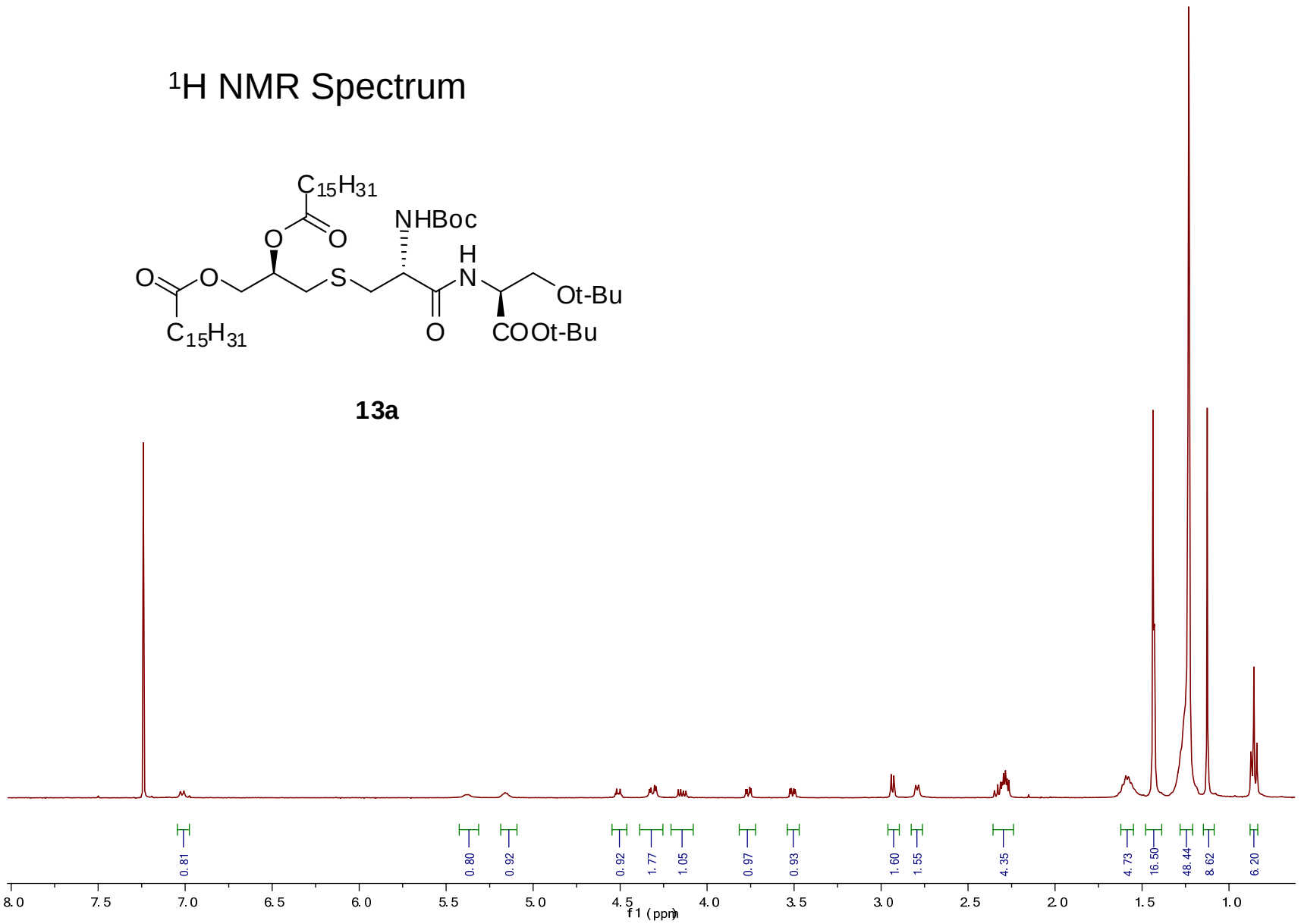
12d

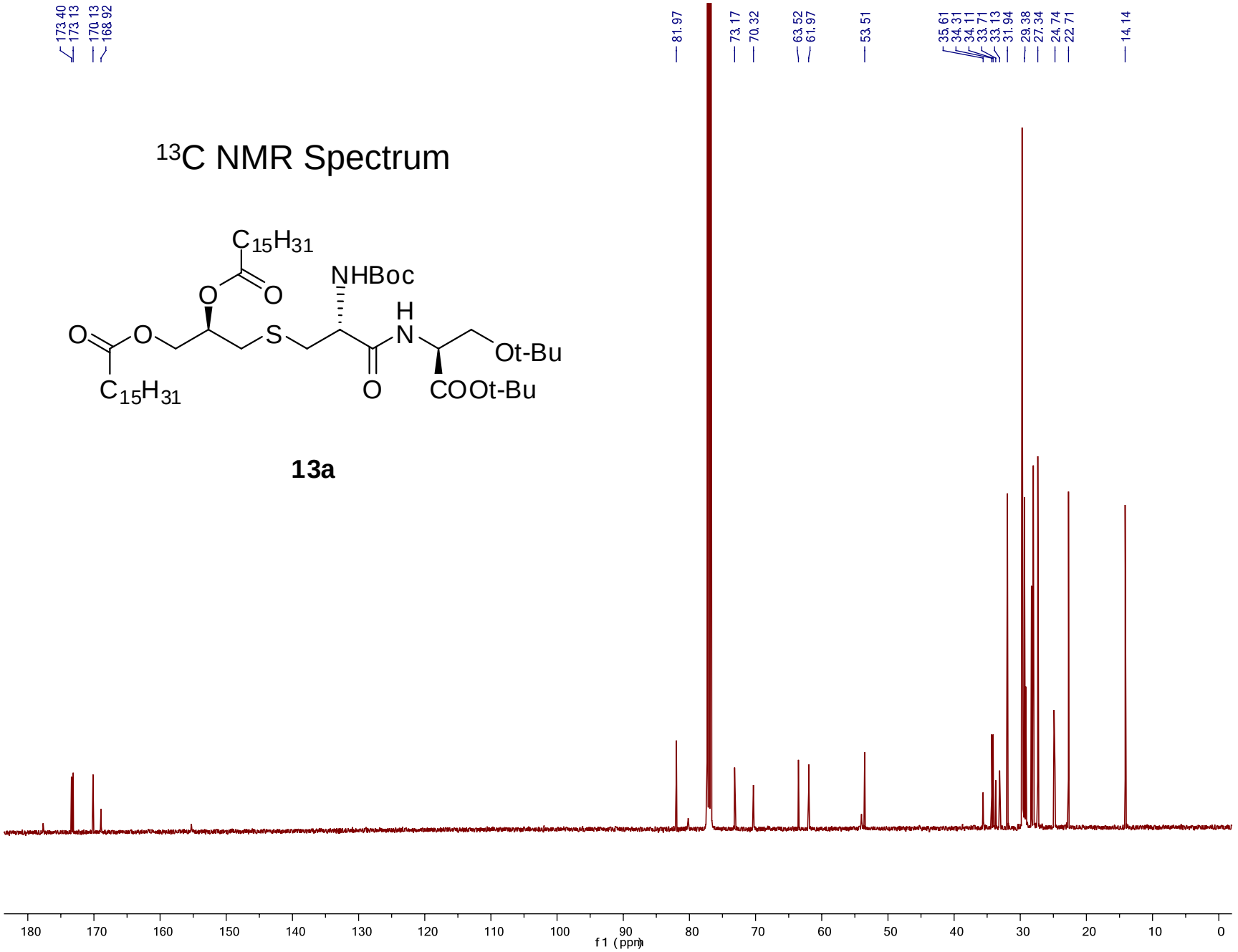


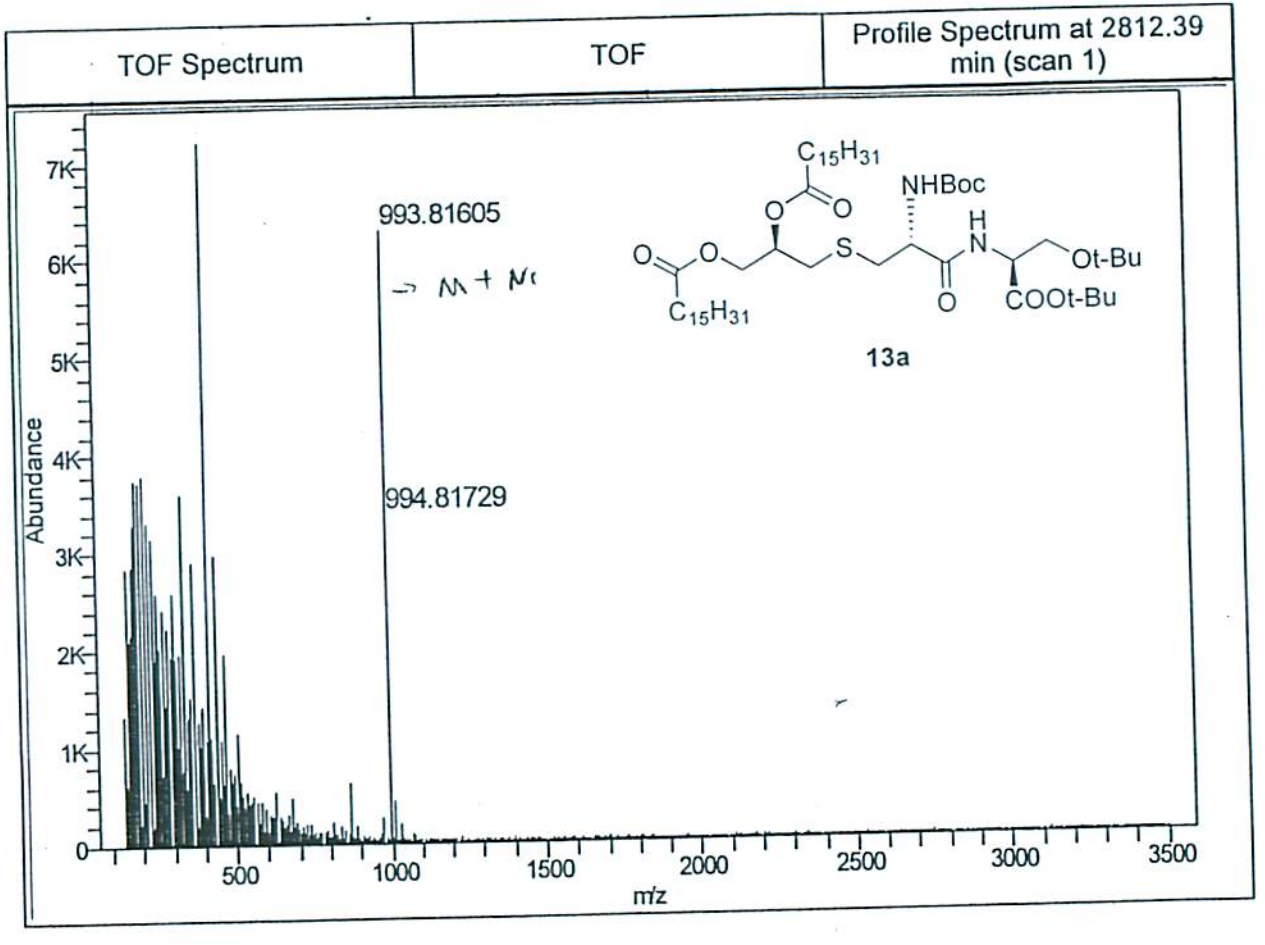

TOF Spectrum
TOF
Profile Spectrum at 26967.68 min (scan 1)
Baseline = 1.50849673202614
Abundance Min = 0
Abundance Max = 701652
515.33934
700K
600K
500K
400K
300K
200K
100K
0
Abundance
500
1000
1500
2000
2500
3000
m/z
NHBoc
O
O
(R)
S
H
N
*
*
Ot-Bu
O
COOCH3
L-Cys-L-Ser 12b
L-Cys-D-Ser 12c
D-Cys-L-Ser 12d

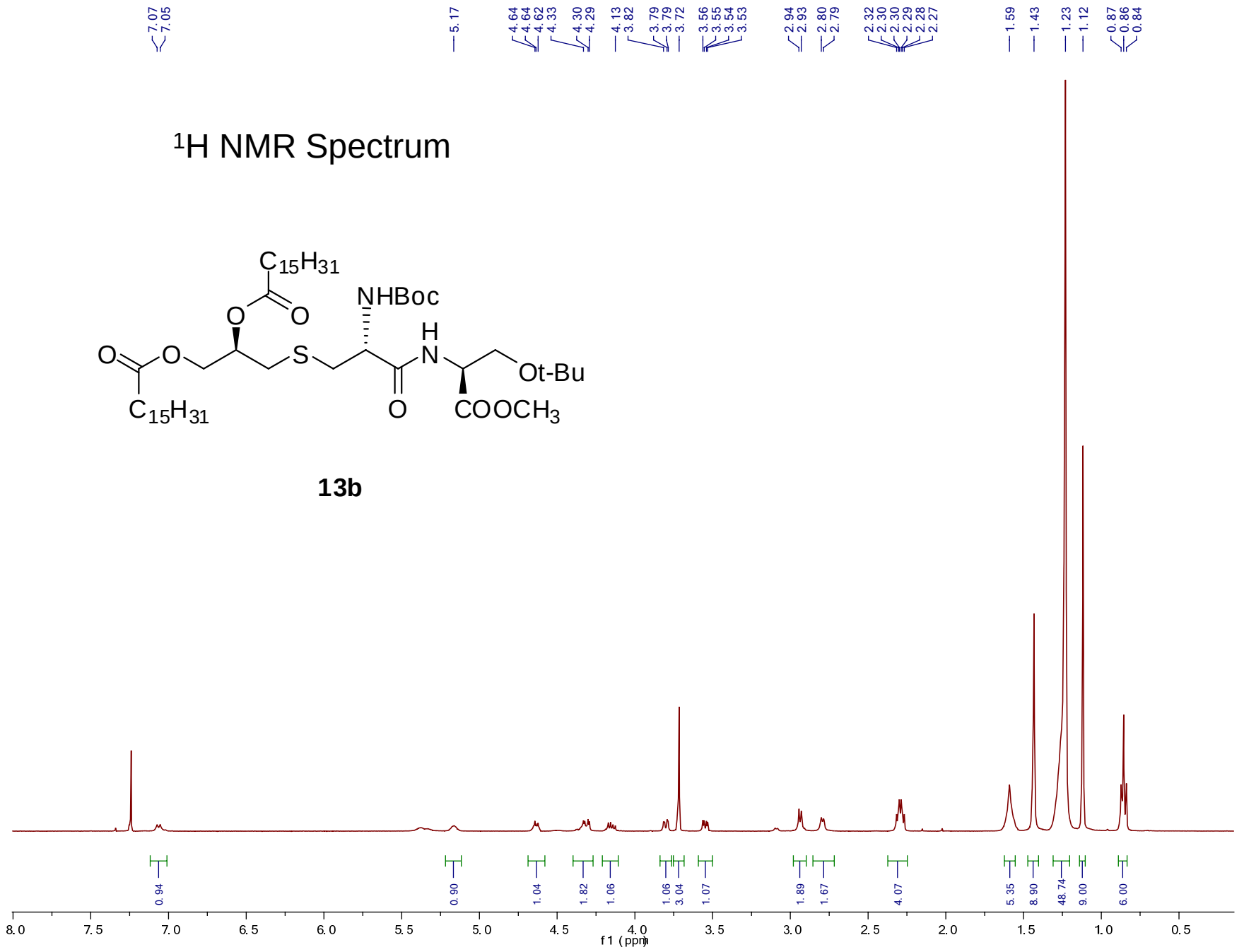
^{1}H NMR Spectrum

13a



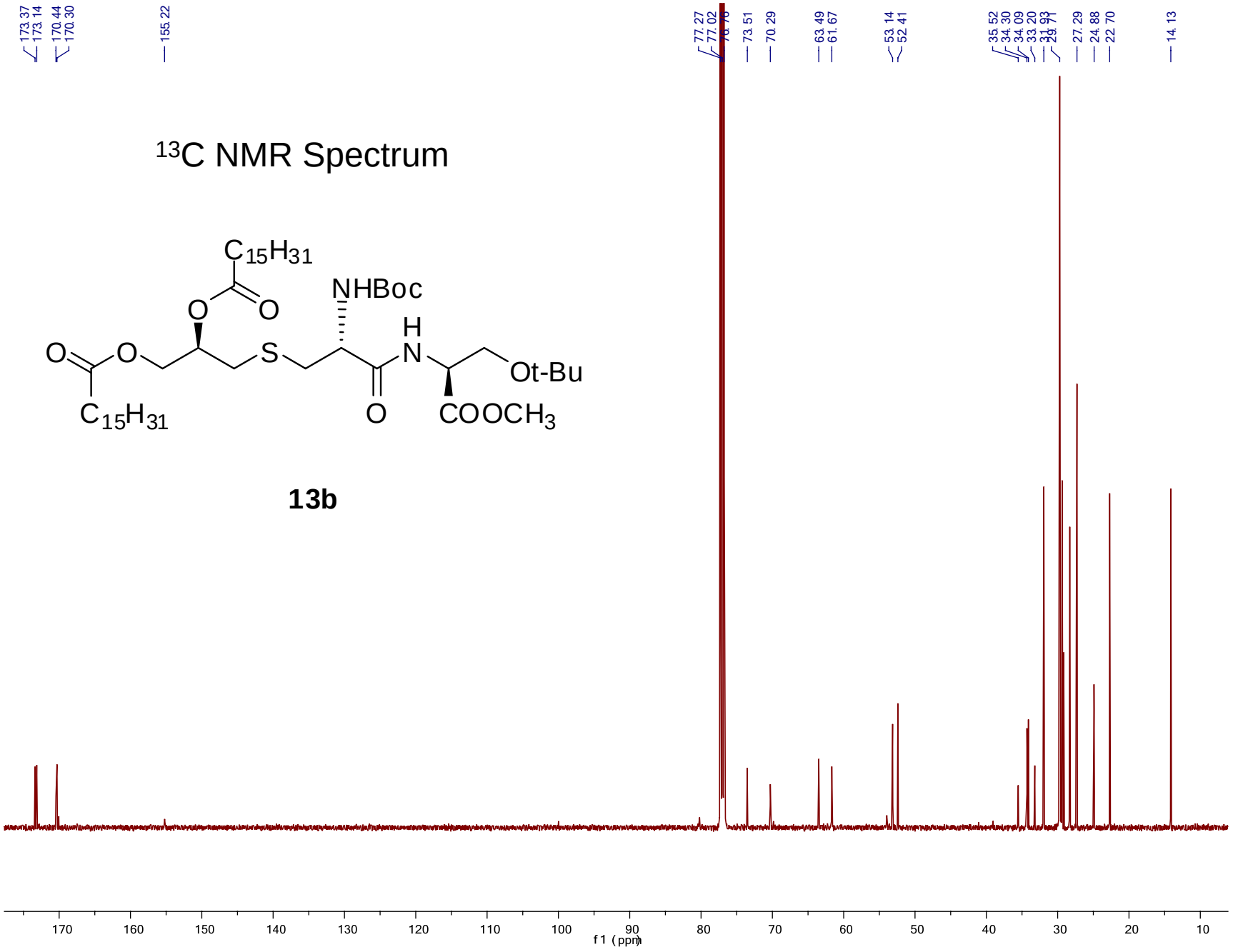

173.40
173.13
170.13
168.92
81.97
73.17
70.32
63.52
61.97
53.51
35.61
34.31
34.11
33.71
33.13
31.94
29.38
27.34
24.74
22.71
14.14
13C NMR Spectrum
C15H31
O
O
NHBoc
H
N
O
O
S
Ot-Bu
C15H31
O
COOt-Bu
13a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

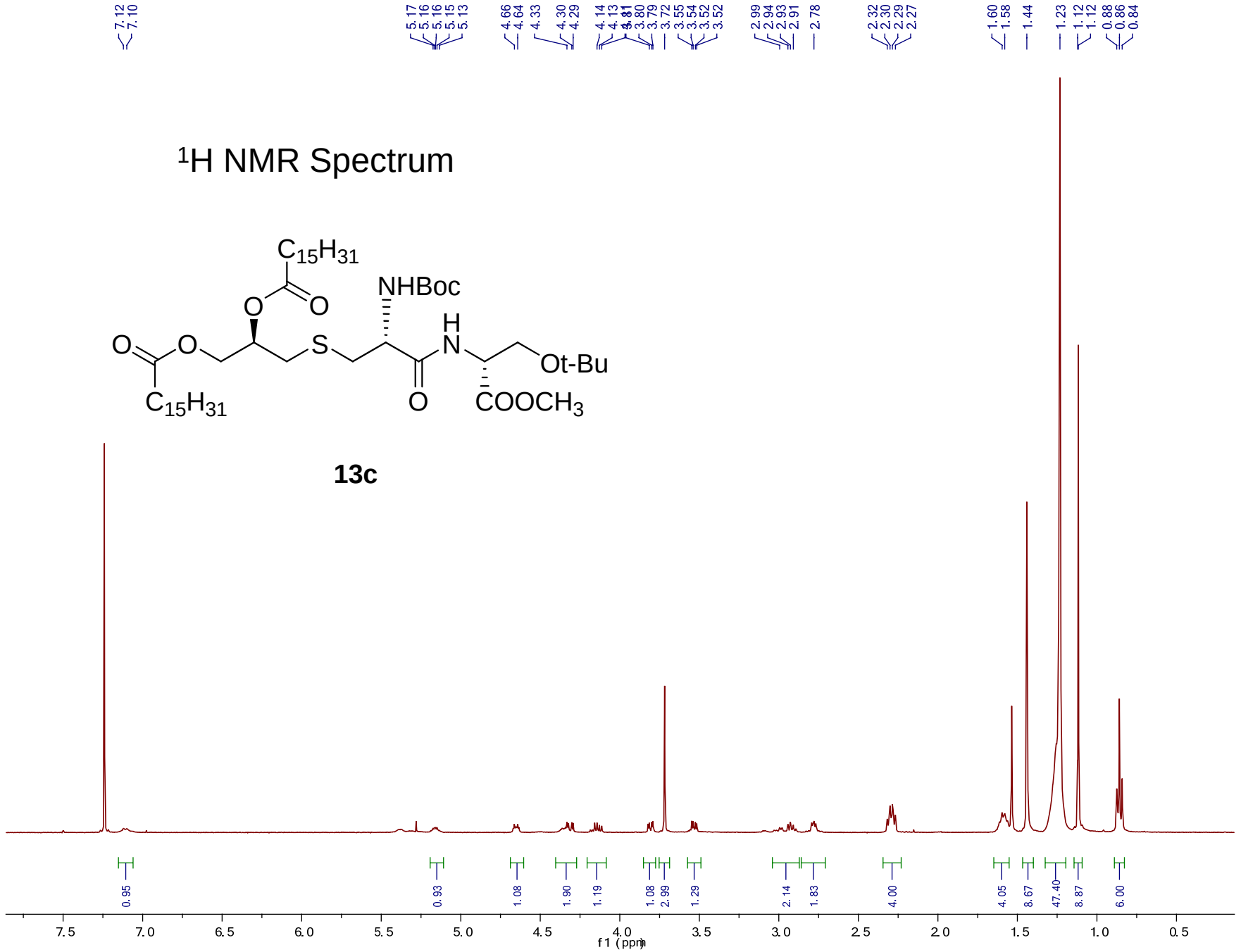

TOF Spectrum
TOF
Profile Spectrum at 2812.39 min (scan 1)
993.81605
994.81729
Abundance
m/z
7K
6K
5K
4K
3K
2K
1K
0
500
1000
1500
2000
2500
3000
3500
C15H31
NHBoc
Ot-Bu
COOt-Bu
13a



^{1}H NMR Spectrum

13b


173.37
173.14
170.44
170.30
155.22
77.27
77.02
76.76
73.51
70.29
63.49
61.67
53.14
52.41
35.52
34.30
34.09
33.20
31.93
29.71
27.29
24.88
22.70
14.13
13C NMR Spectrum
C15H31
O
O
NHBoc
H
N
O
O
S
Ot-Bu
C15H31
O
COOCH3
13b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

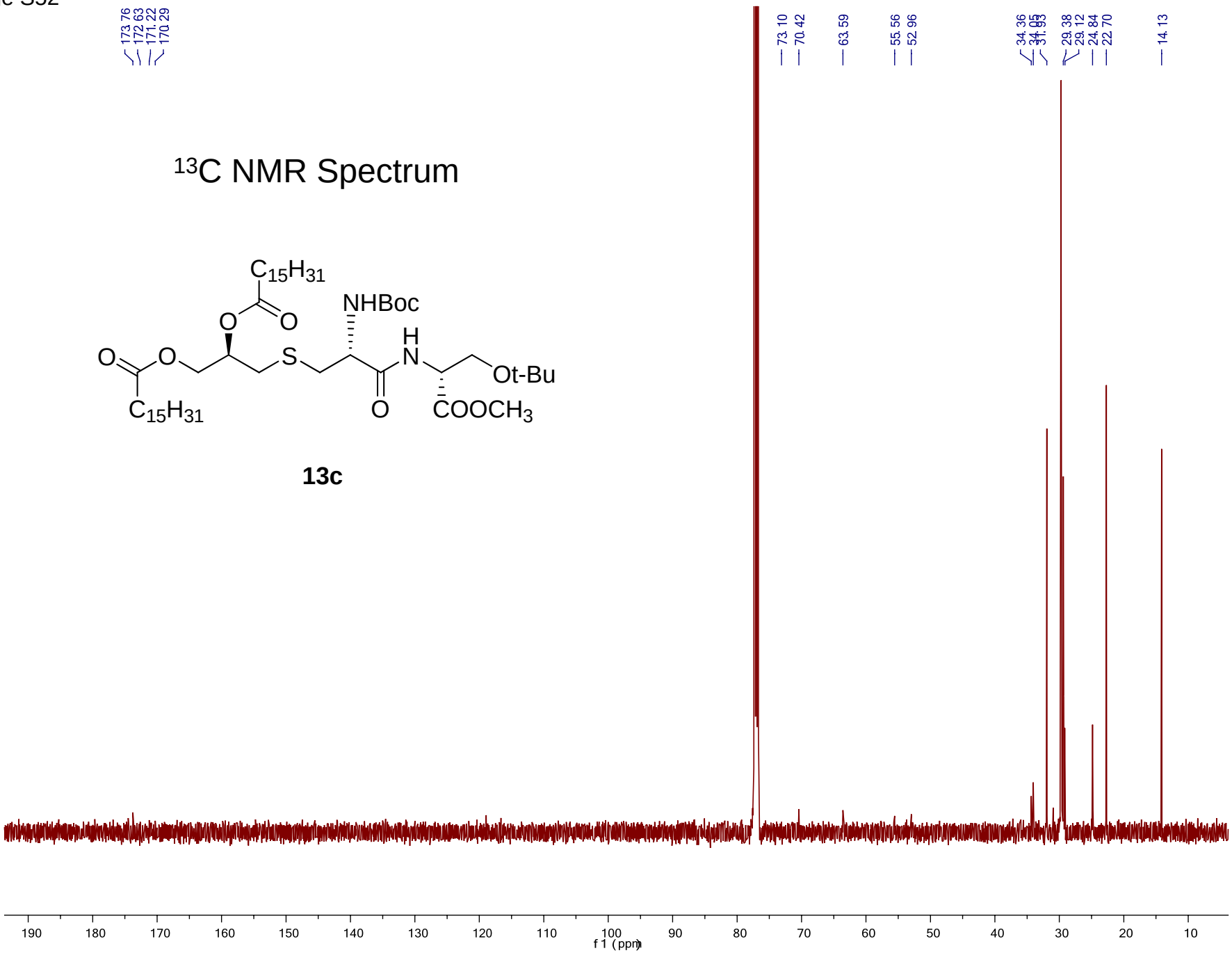


^{1}H NMR Spectrum

13c

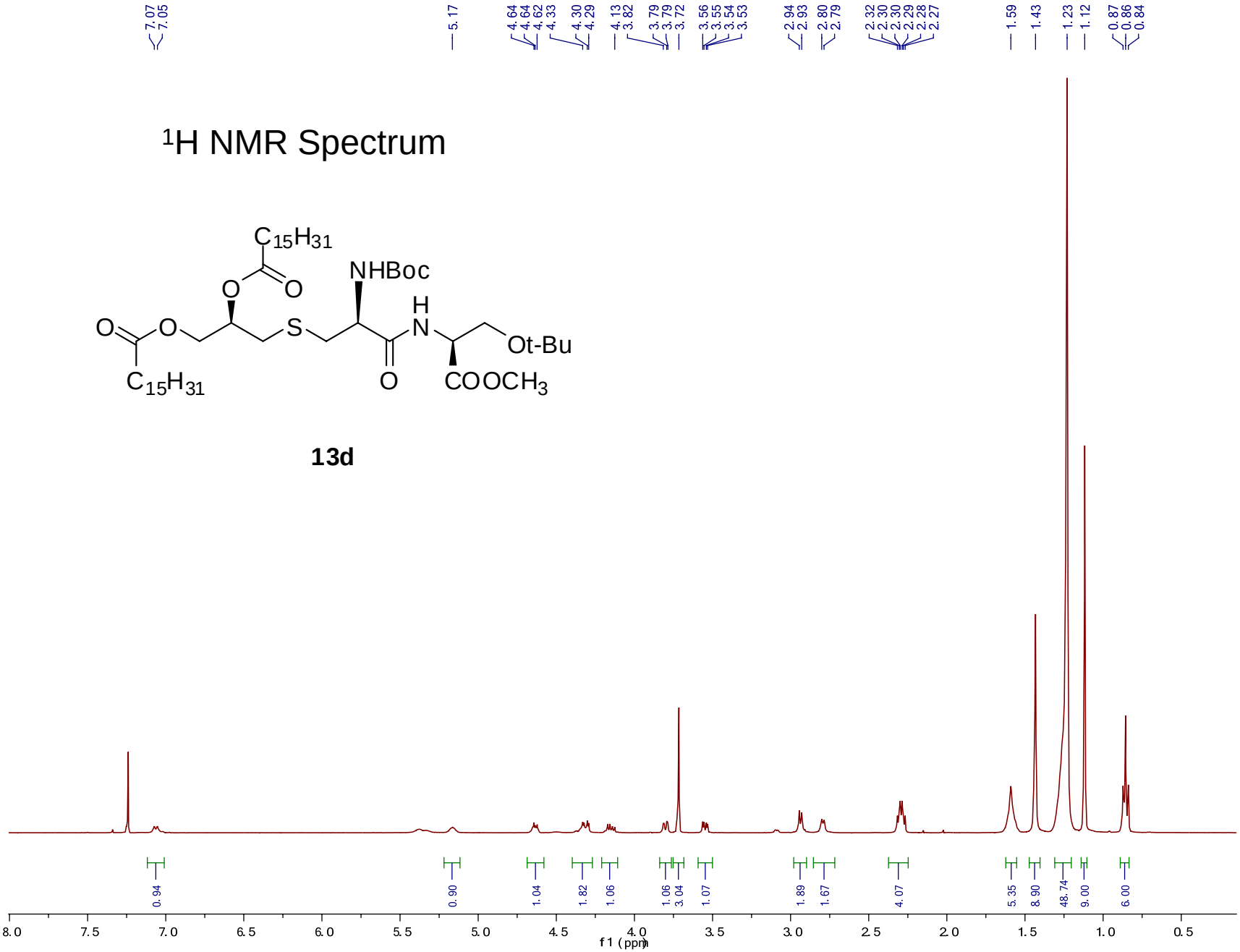
^{13}C NMR Spectrum

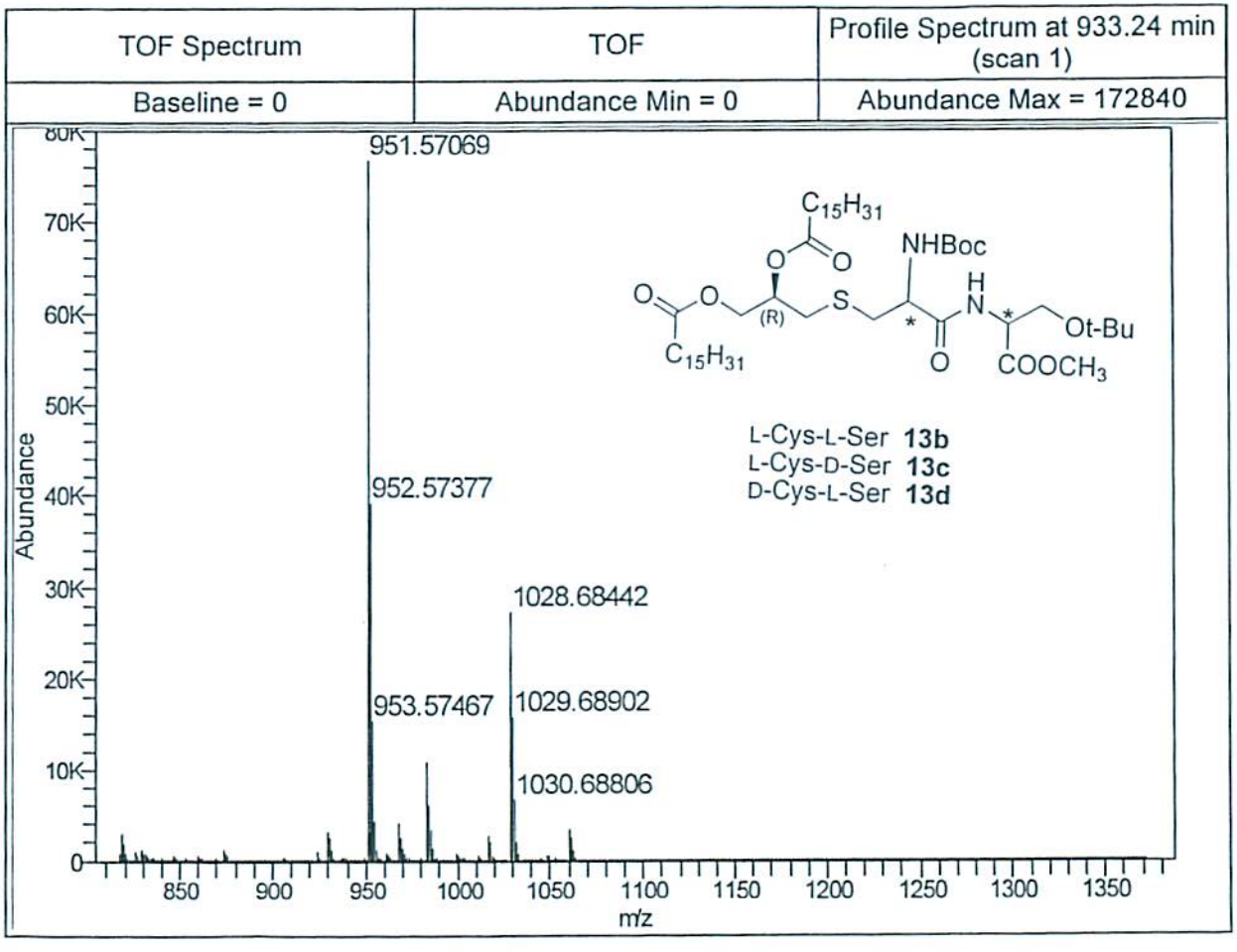
13c



^{1}H NMR Spectrum

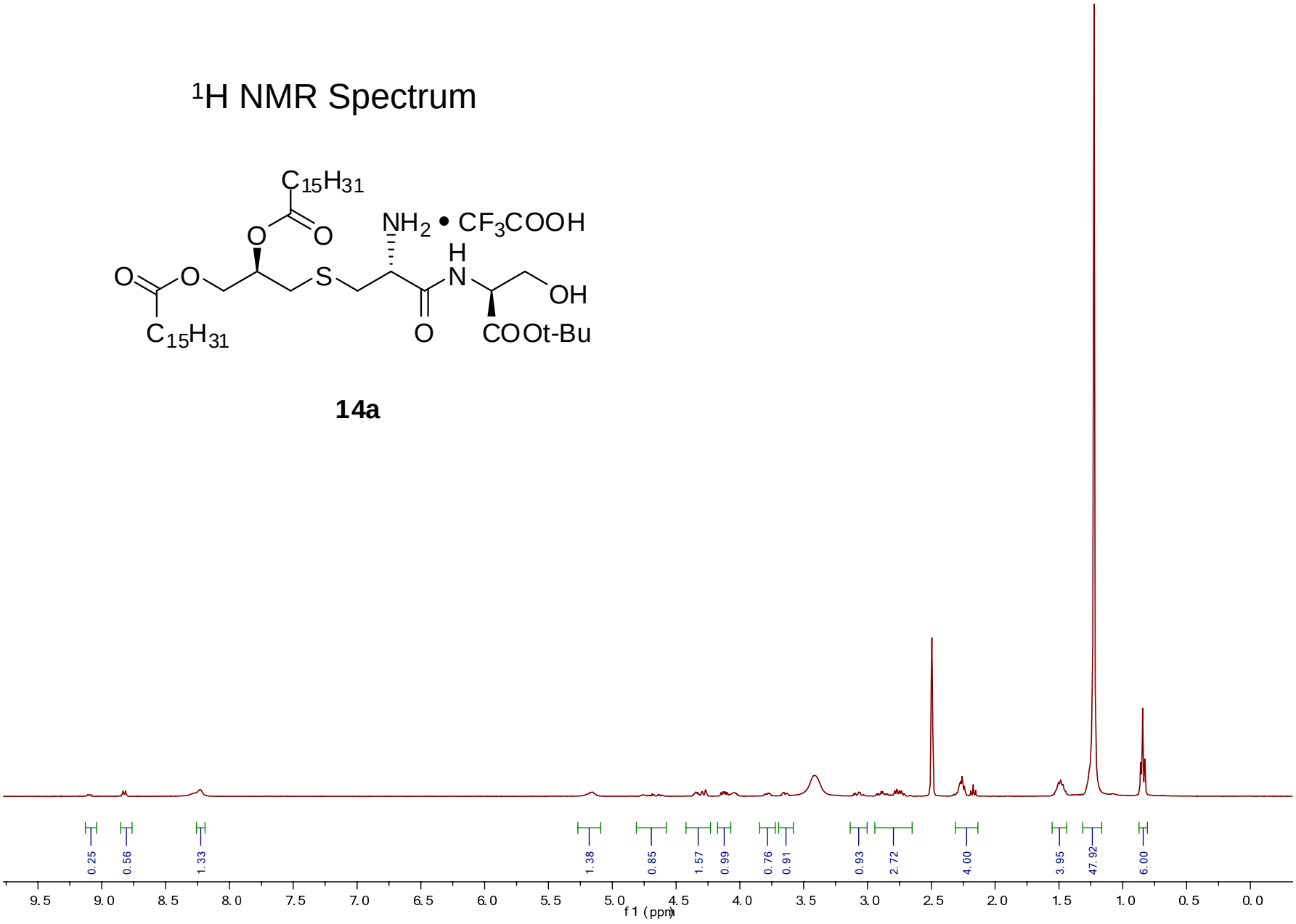
13d




TOF Spectrum
TOF
Profile Spectrum at 933.24 min (scan 1)
Baseline = 0
Abundance Min = 0
Abundance Max = 172840
951.57069
952.57377
953.57467
1028.68442
1029.68902
1030.68806
Abundance
m/z
L-Cys-L-Ser 13b
L-Cys-D-Ser 13c
D-Cys-L-Ser 13d

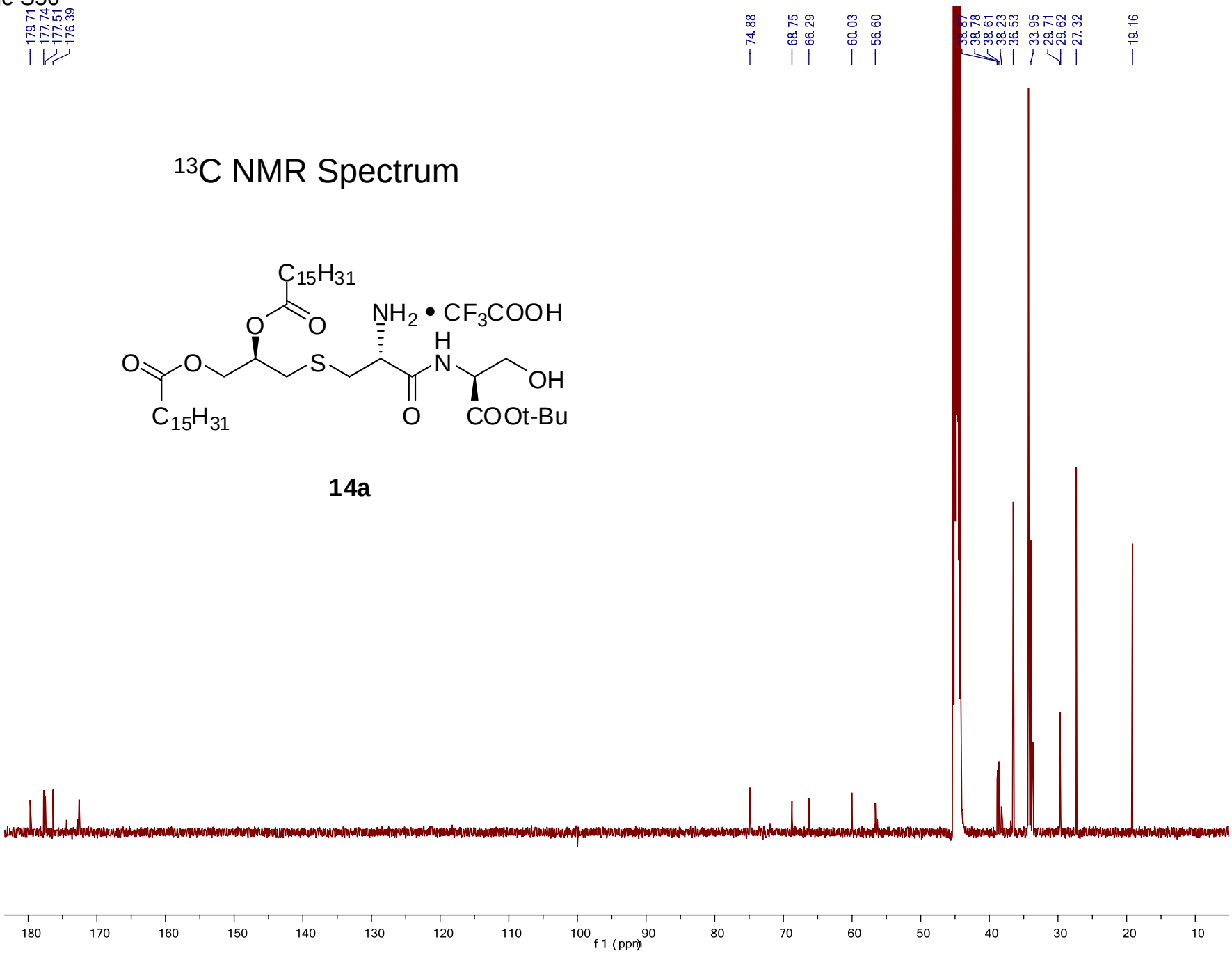
^{1}H NMR Spectrum

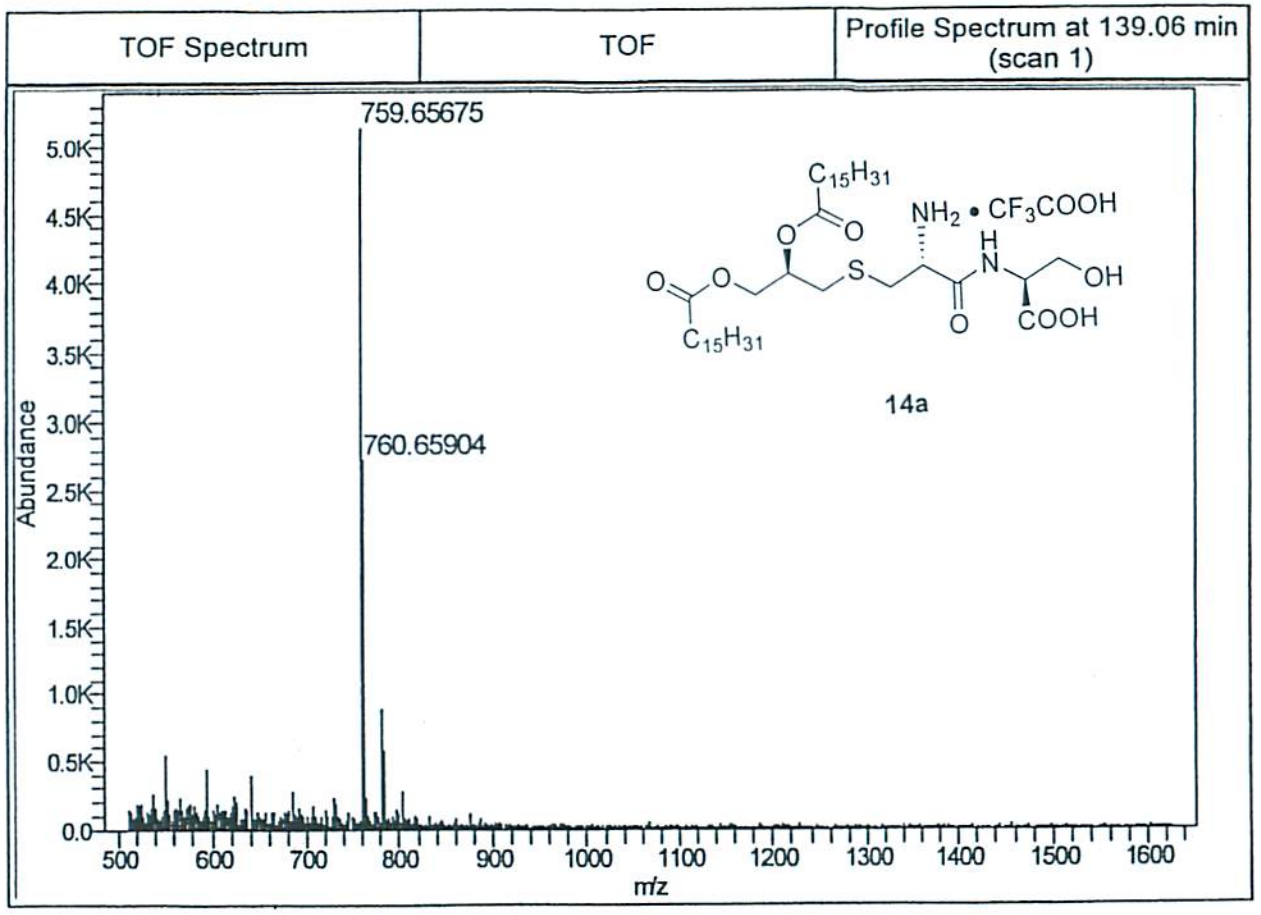
14a



^{13}C NMR Spectrum

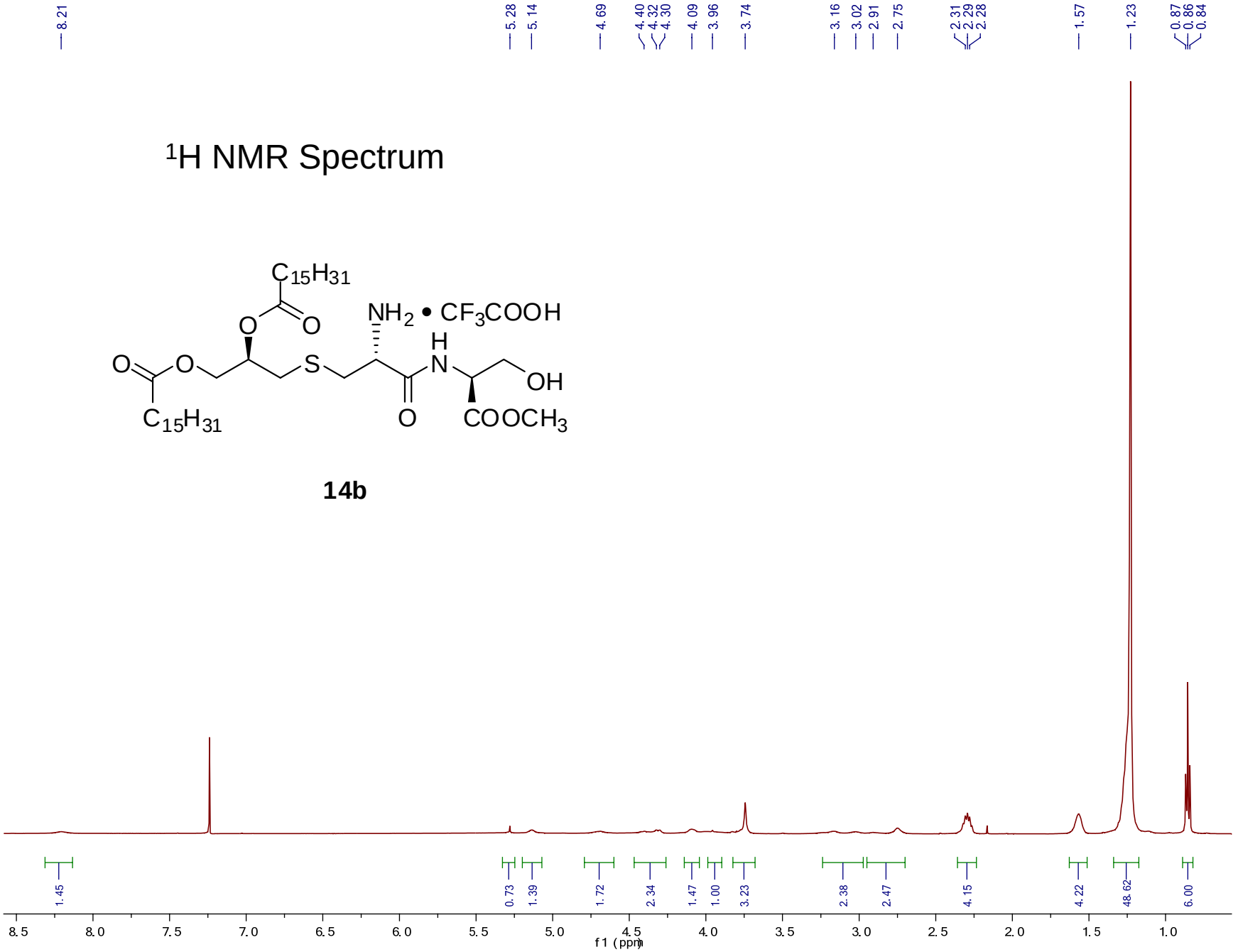
14a

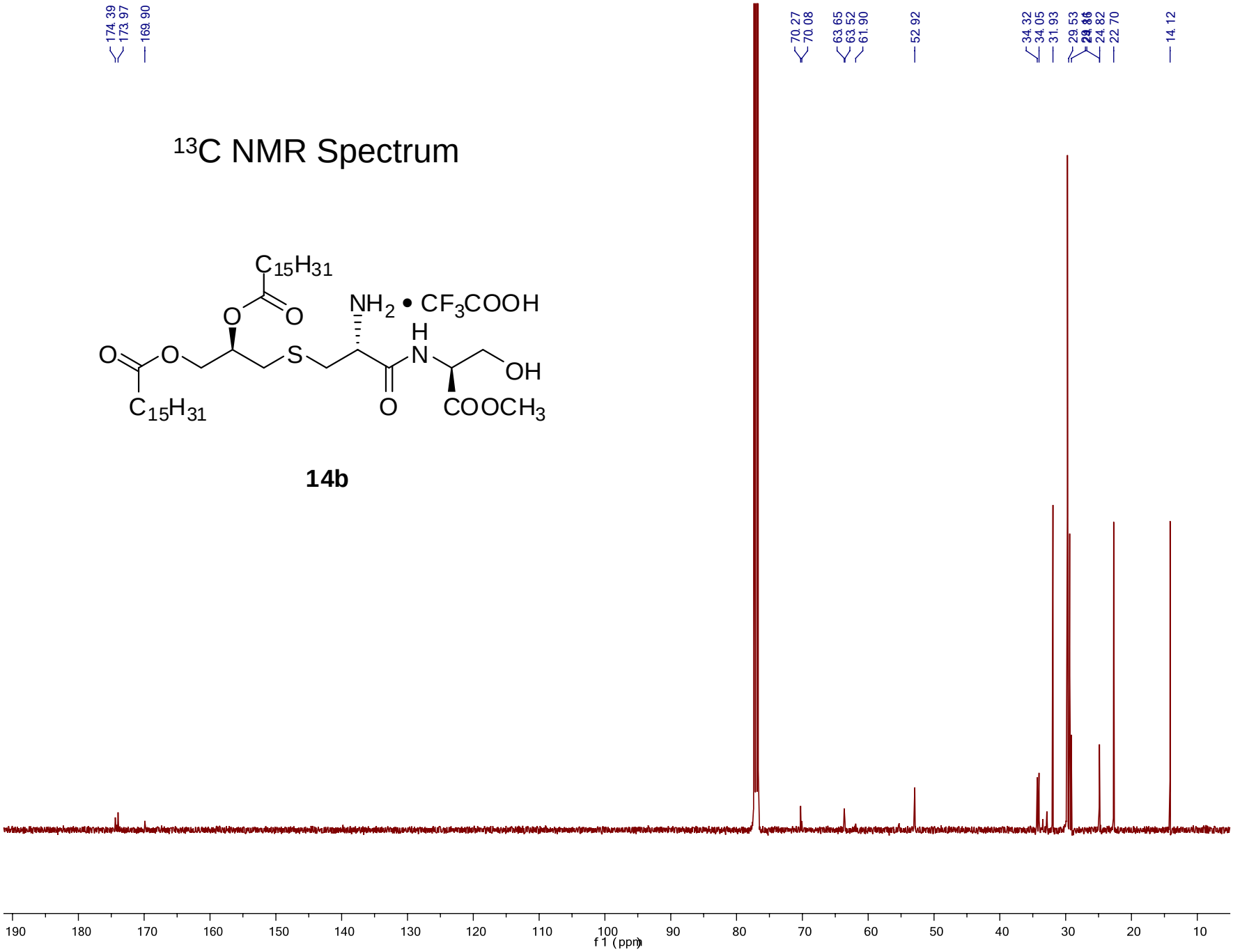



TOF Spectrum
TOF
Profile Spectrum at 139.06 min (scan 1)
759.65675
760.65904
Abundance
m/z
14a

^{1}H NMR Spectrum

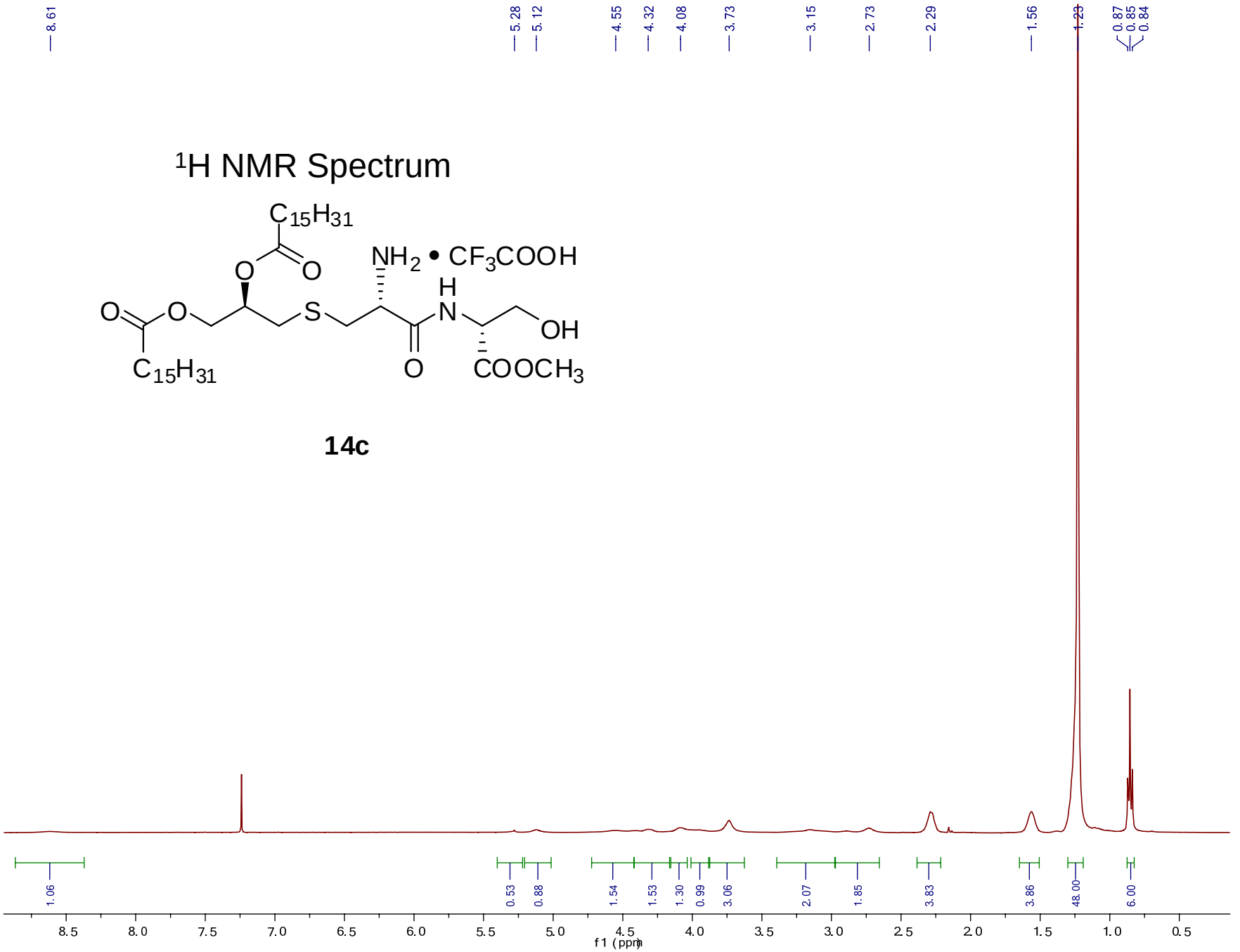
14b

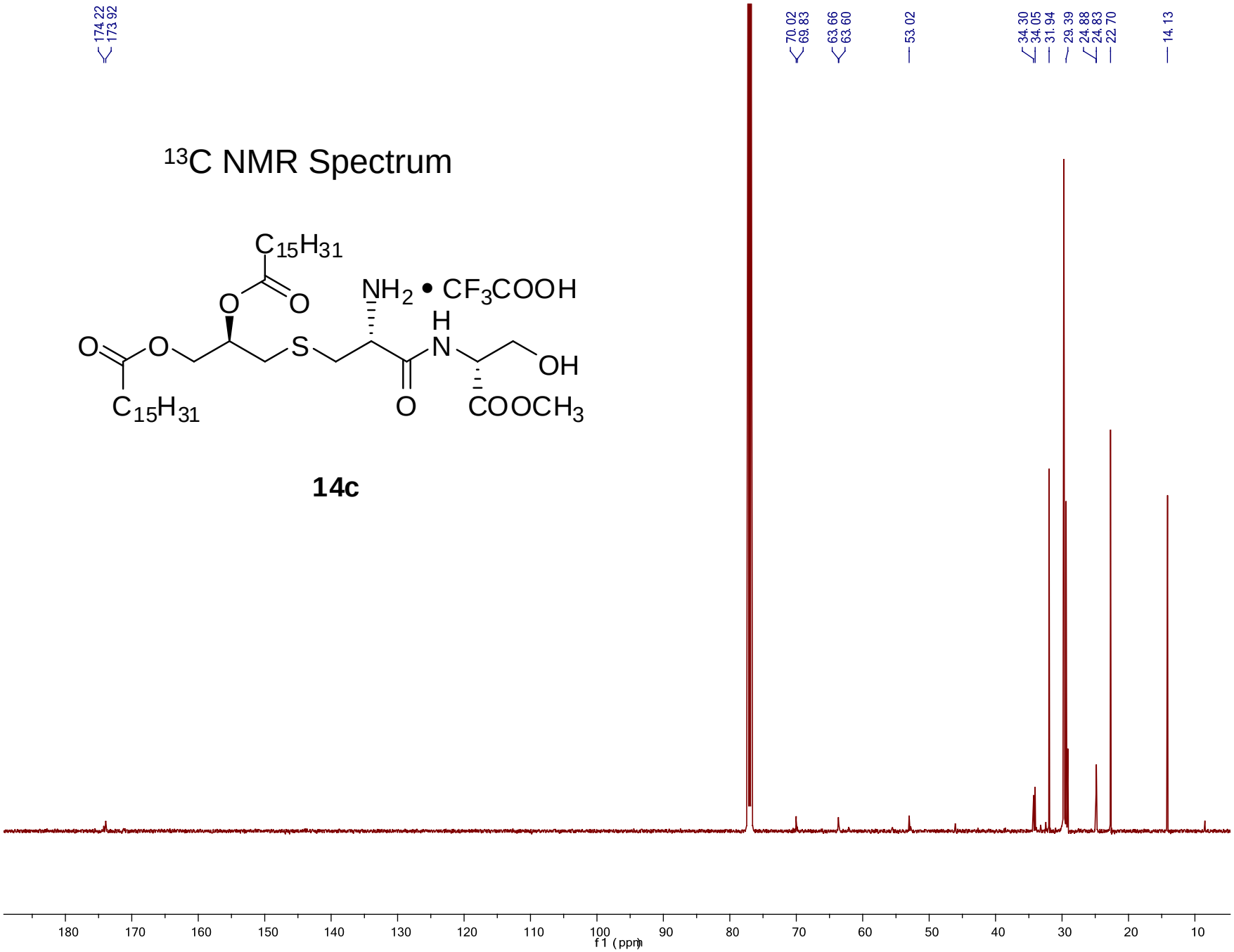



174.39
173.97
169.90
70.27
70.08
63.65
63.52
61.90
52.92
34.32
34.05
31.93
29.53
24.82
22.70
14.12
13C NMR Spectrum
C15H31
O
O
NH2 • CF3COOH
H
O
O
S
N
OH
C15H31
O
COOCH3
14b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

^{1}H NMR Spectrum

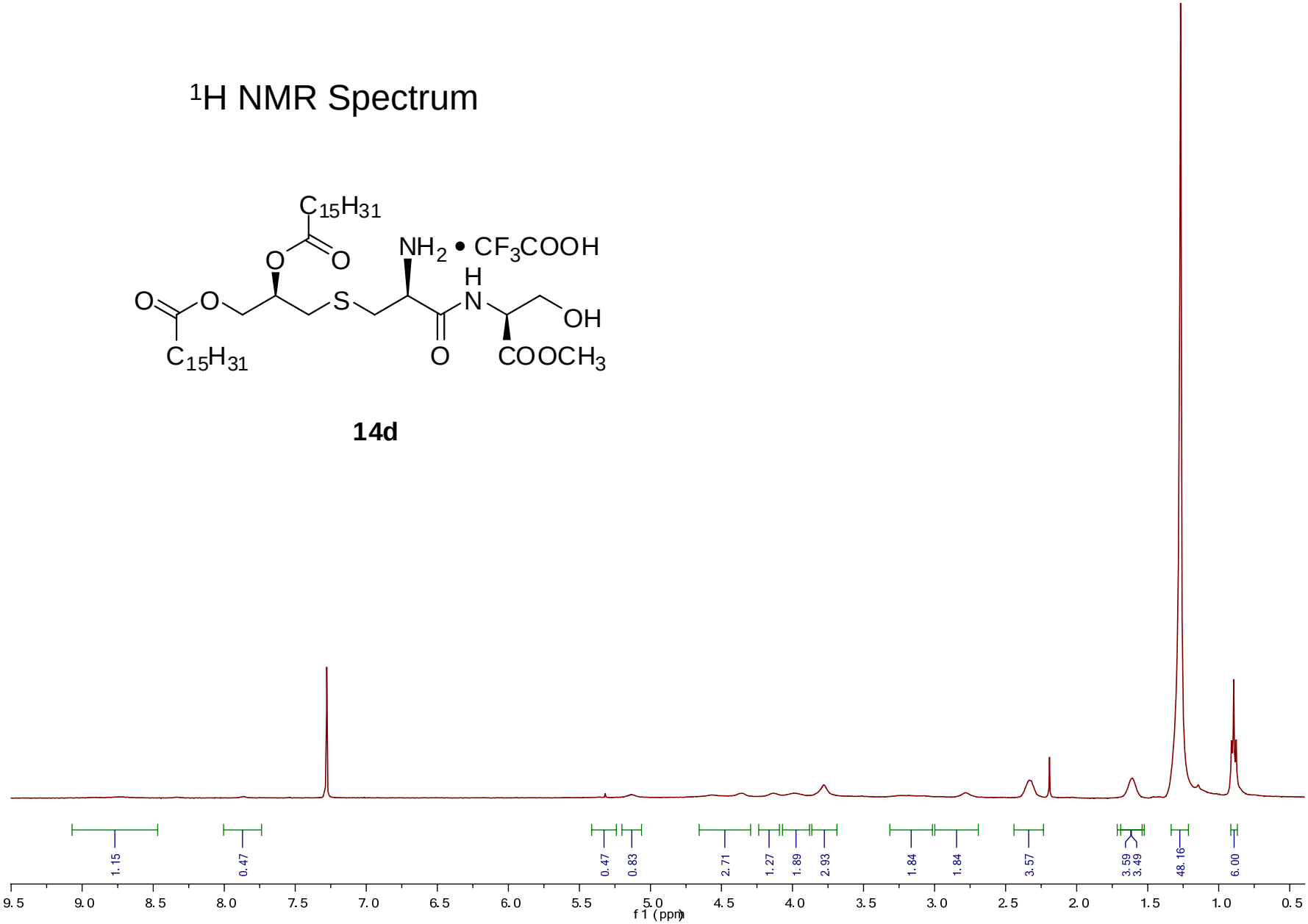
14c




174.22
173.92
70.02
69.83
63.66
63.60
53.02
34.30
34.05
31.94
29.39
24.88
24.83
22.70
14.13
13C NMR Spectrum
C15H31
O
O
NH2 • CF3COOH
H
O
O
S
N
OH
C15H31
O
COOCH3
14c
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

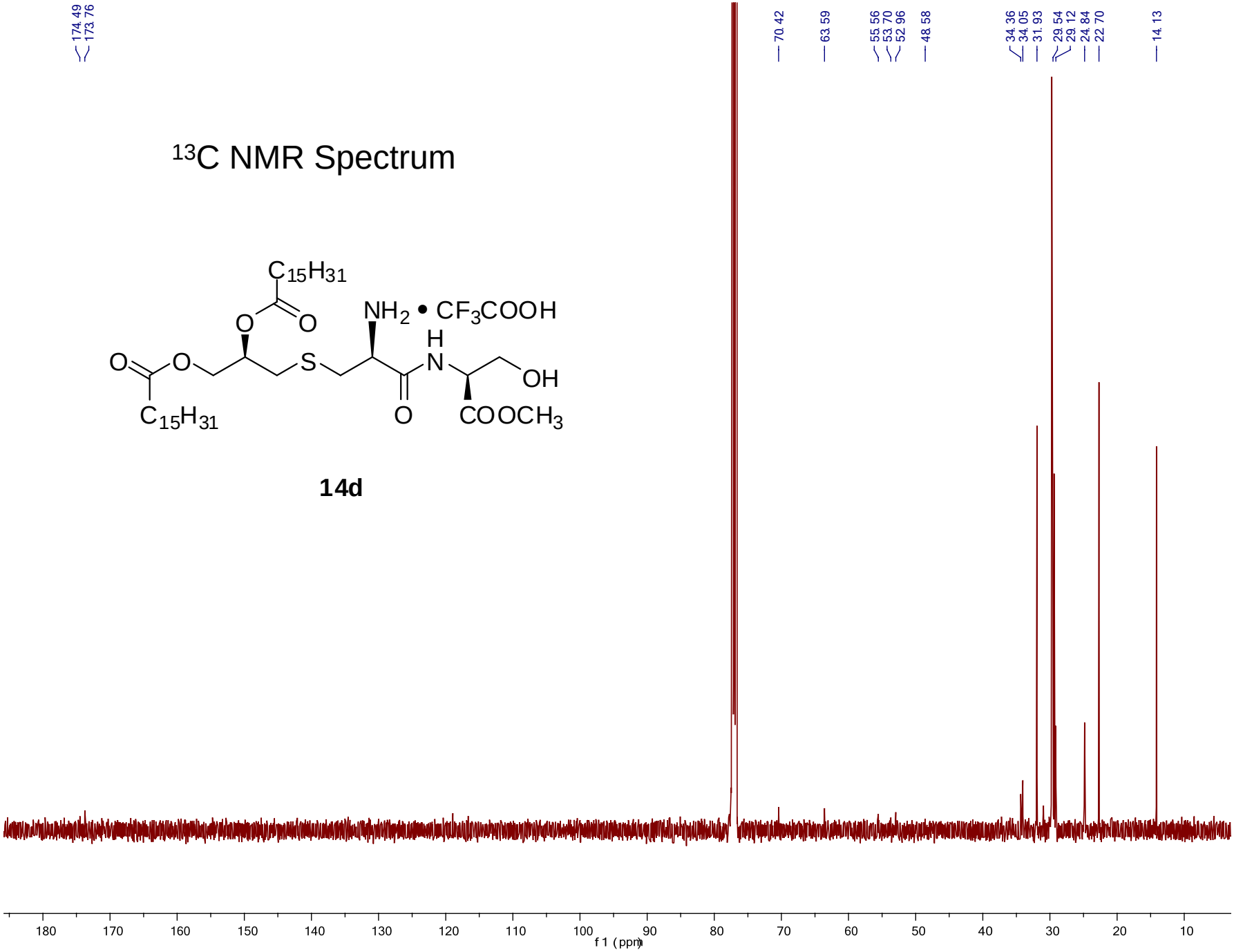
^{1}H NMR Spectrum

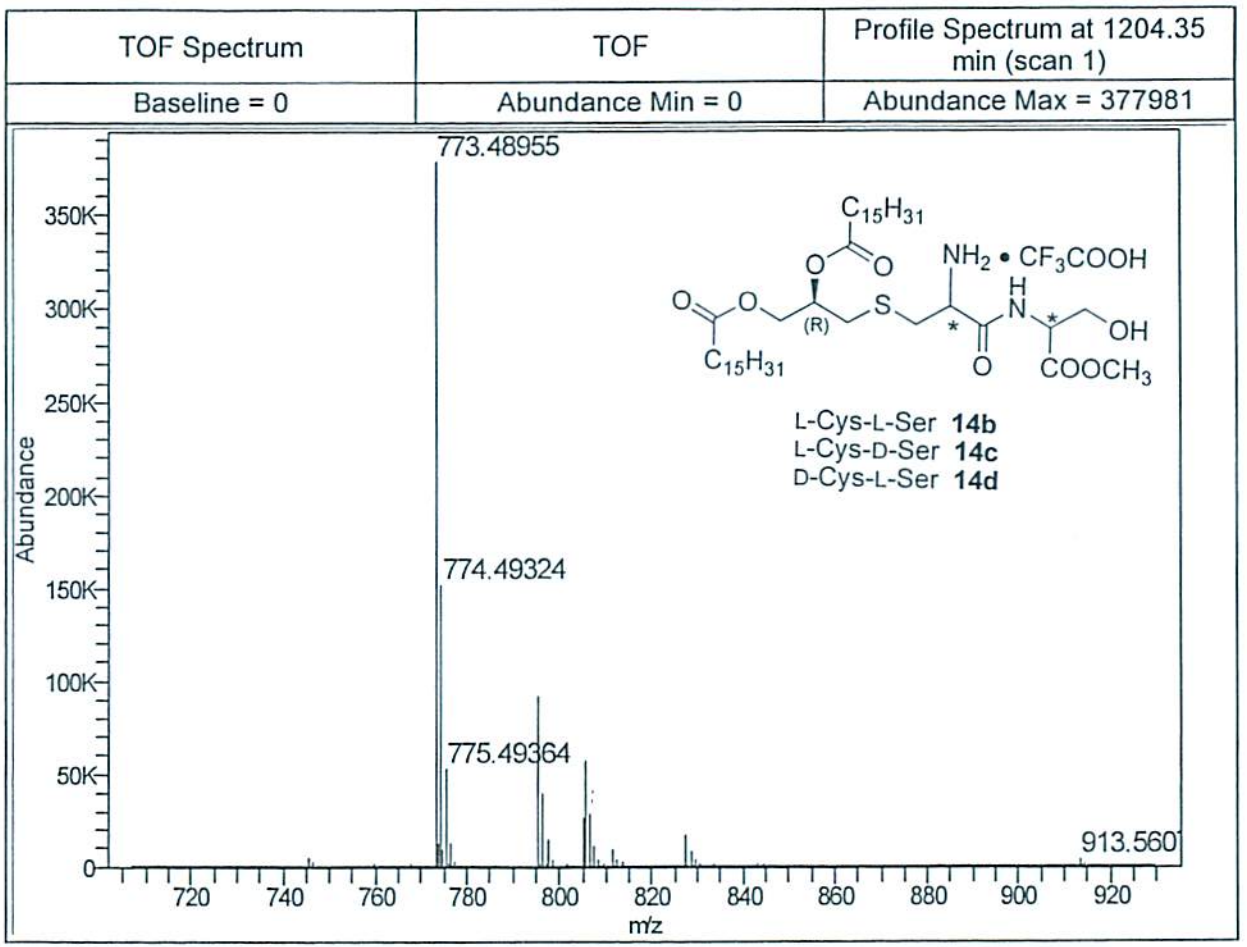
14d

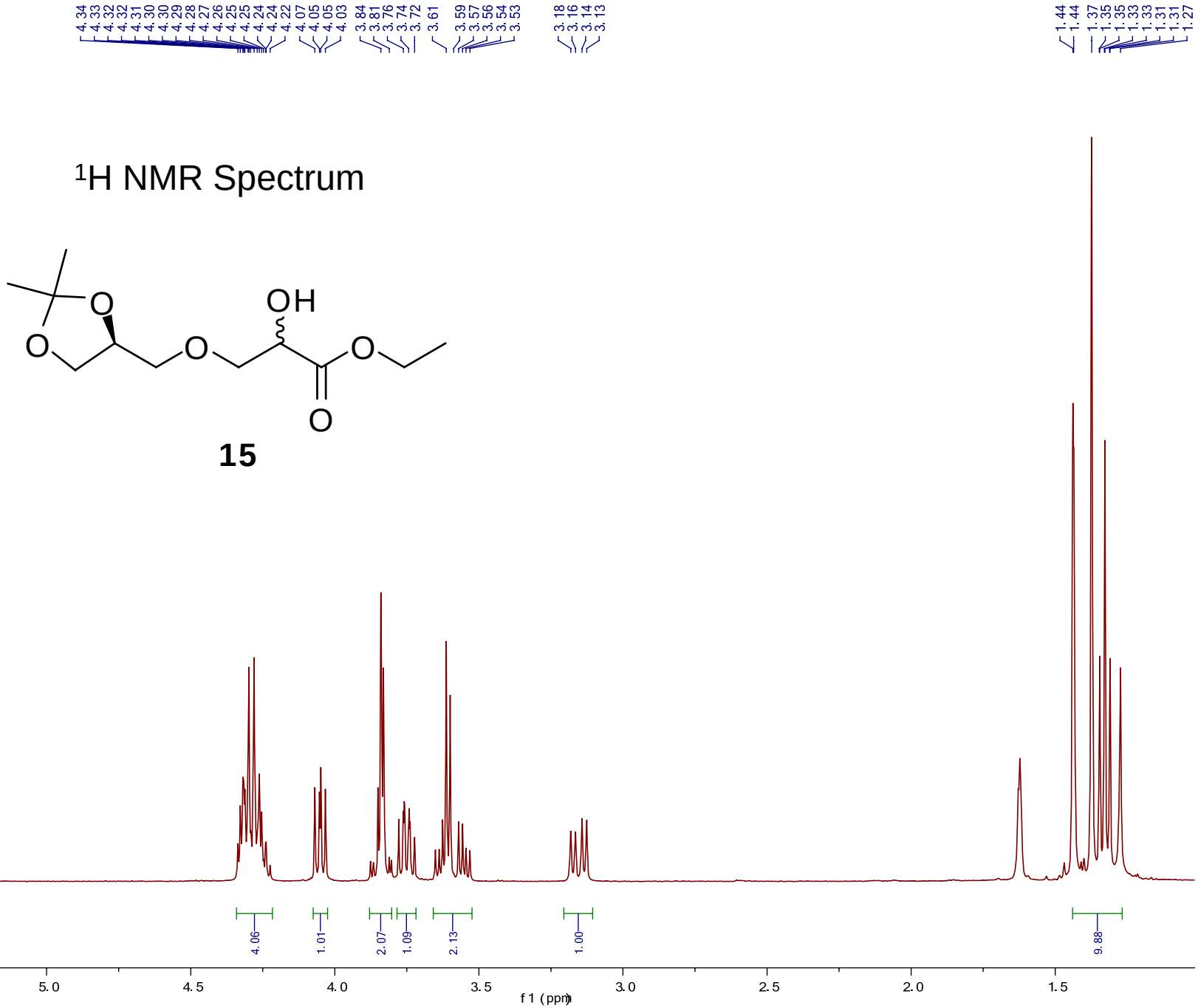


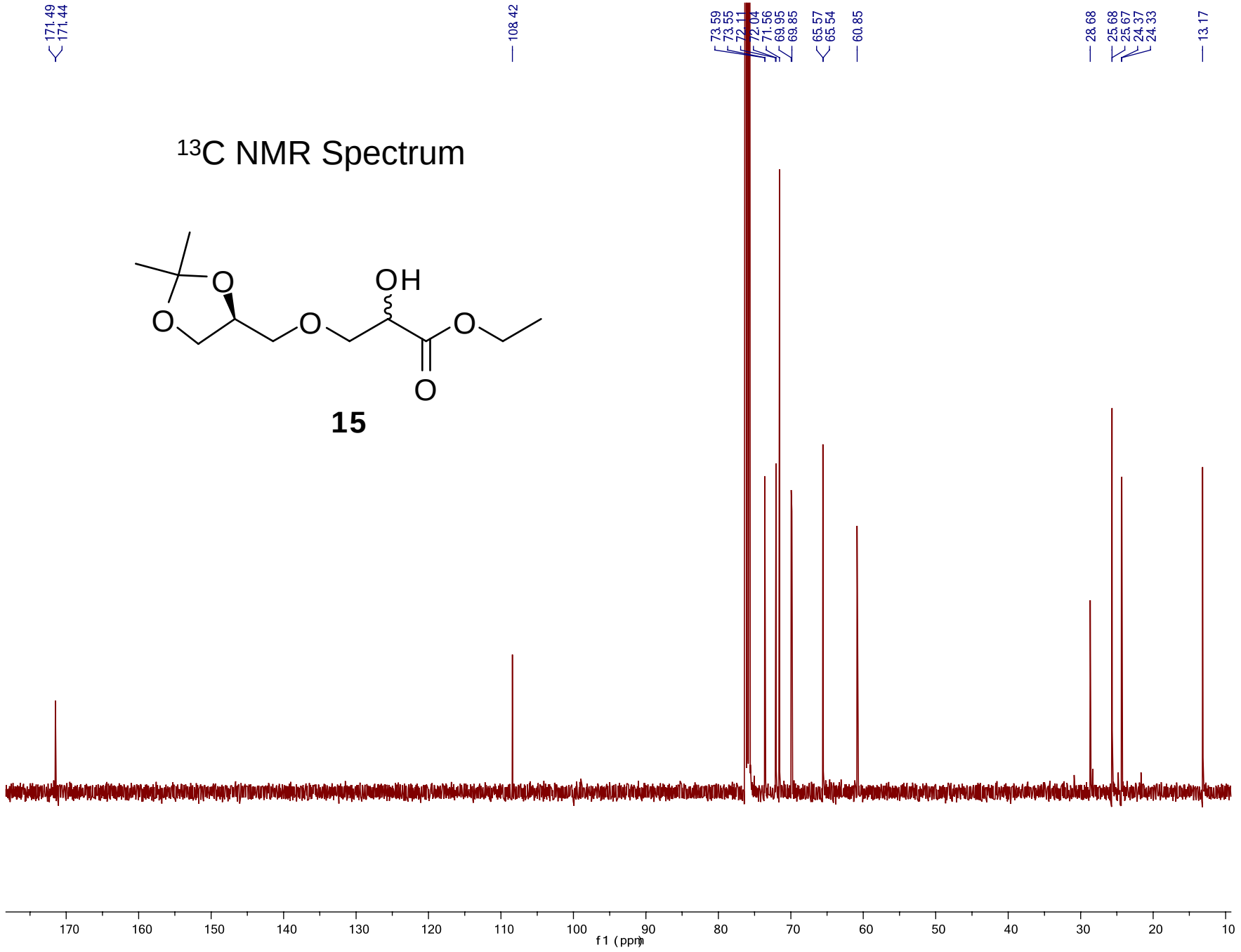
^{13}C NMR Spectrum

14d



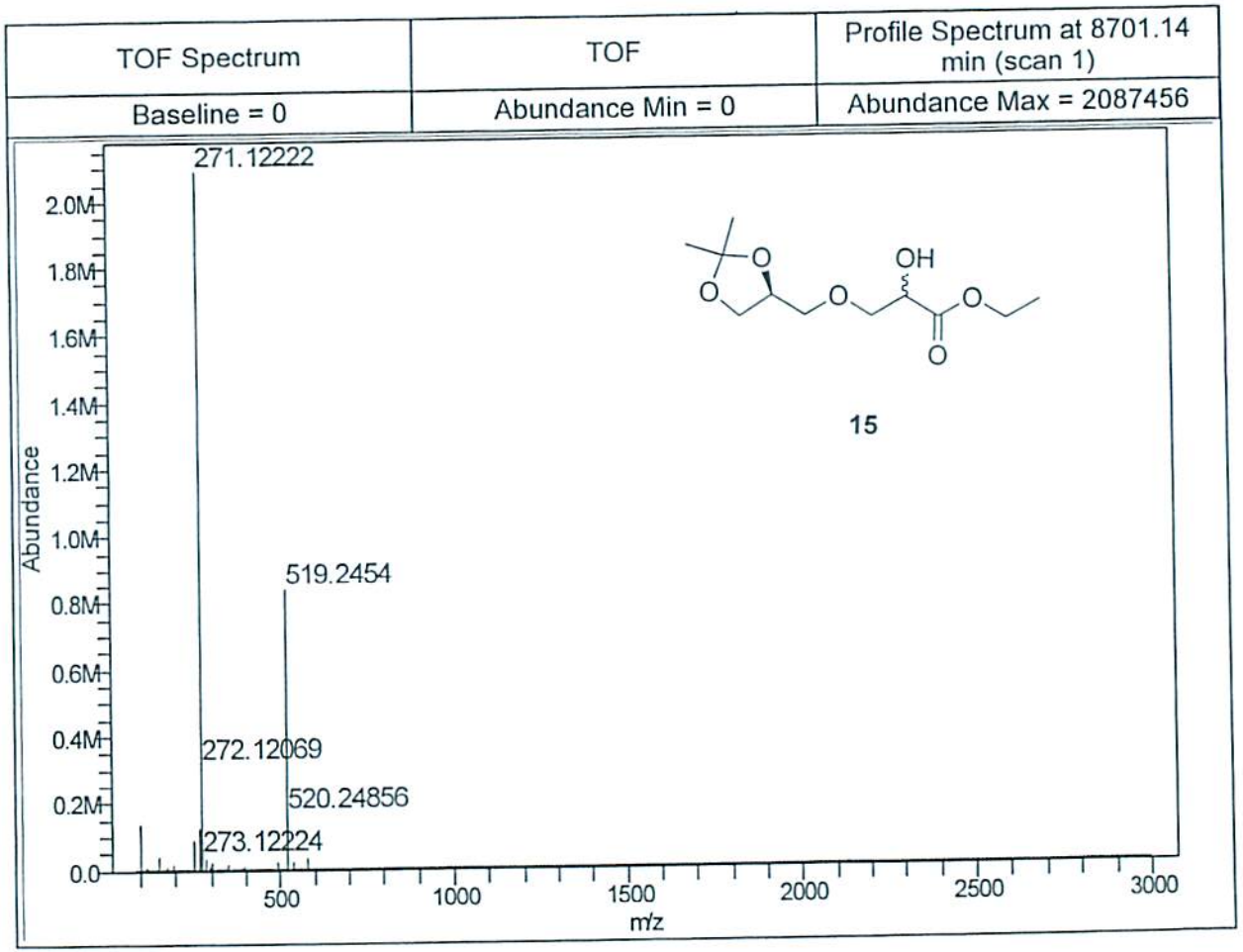

TOF Spectrum
TOF
Profile Spectrum at 1204.35 min (scan 1)
Baseline = 0
Abundance Min = 0
Abundance Max = 377981
773.48955
774.49324
775.49364
913.5601
Abundance
m/z
350K
300K
250K
200K
150K
100K
50K
0
720
740
760
780
800
820
840
860
880
900
920
L-Cys-L-Ser 14b
L-Cys-D-Ser 14c
D-Cys-L-Ser 14d


4.34
4.33
4.32
4.32
4.31
4.30
4.30
4.29
4.28
4.27
4.26
4.25
4.25
4.24
4.24
4.22
4.07
4.05
4.05
4.03
3.84
3.81
3.76
3.74
3.72
3.61
3.59
3.57
3.56
3.54
3.53
3.18
3.16
3.14
3.13
1.44
1.44
1.37
1.35
1.35
1.33
1.31
1.31
1.27
1H NMR Spectrum
O
O
OH
O
O
O
15
4.06
1.01
2.07
1.09
2.13
1.00
9.88
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

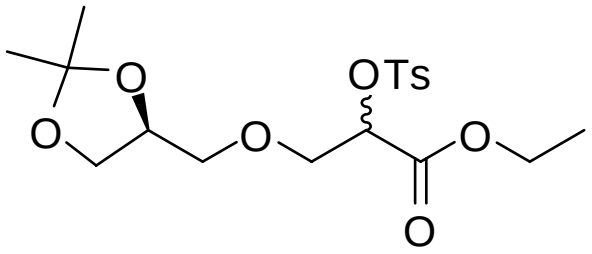


^{13}C NMR Spectrum

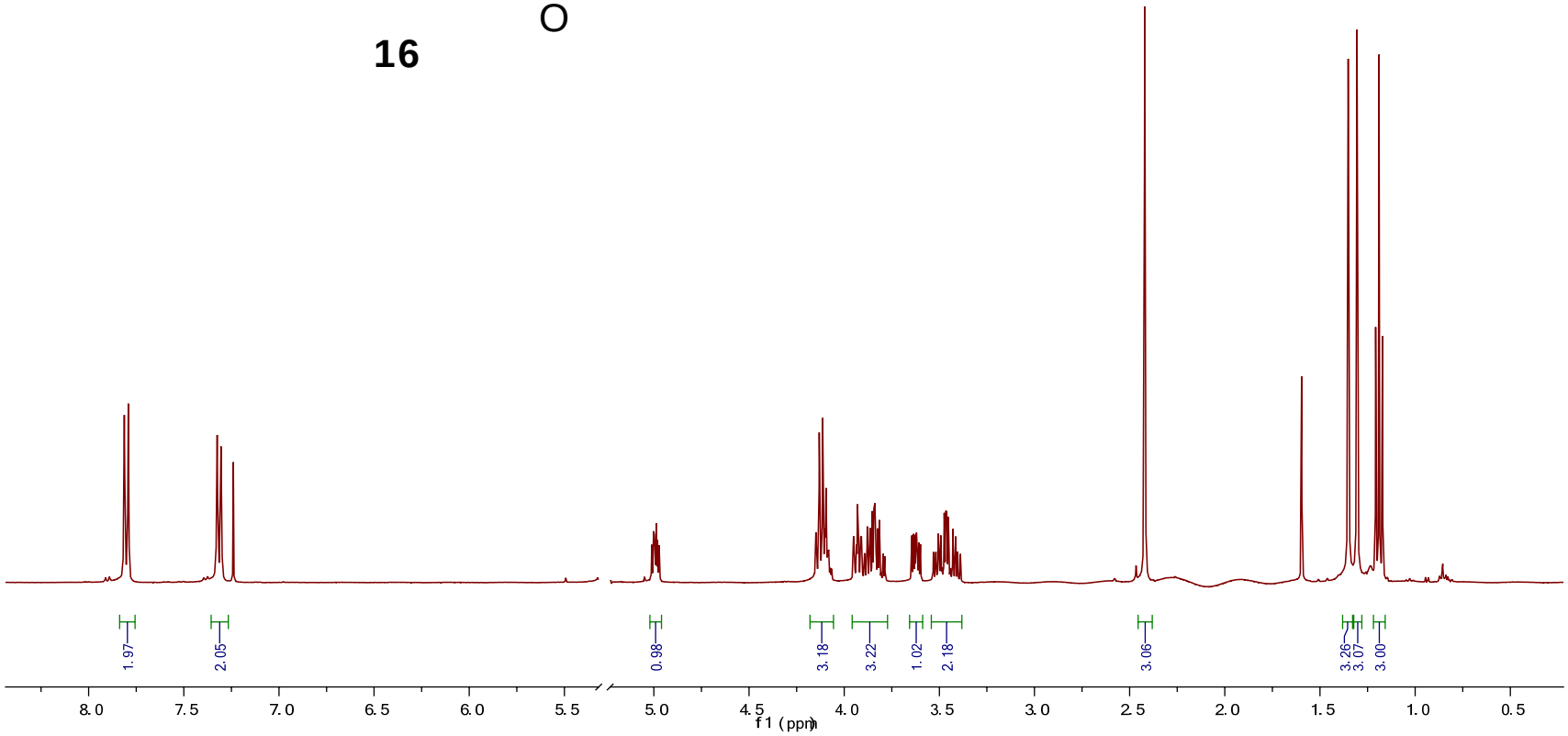
15

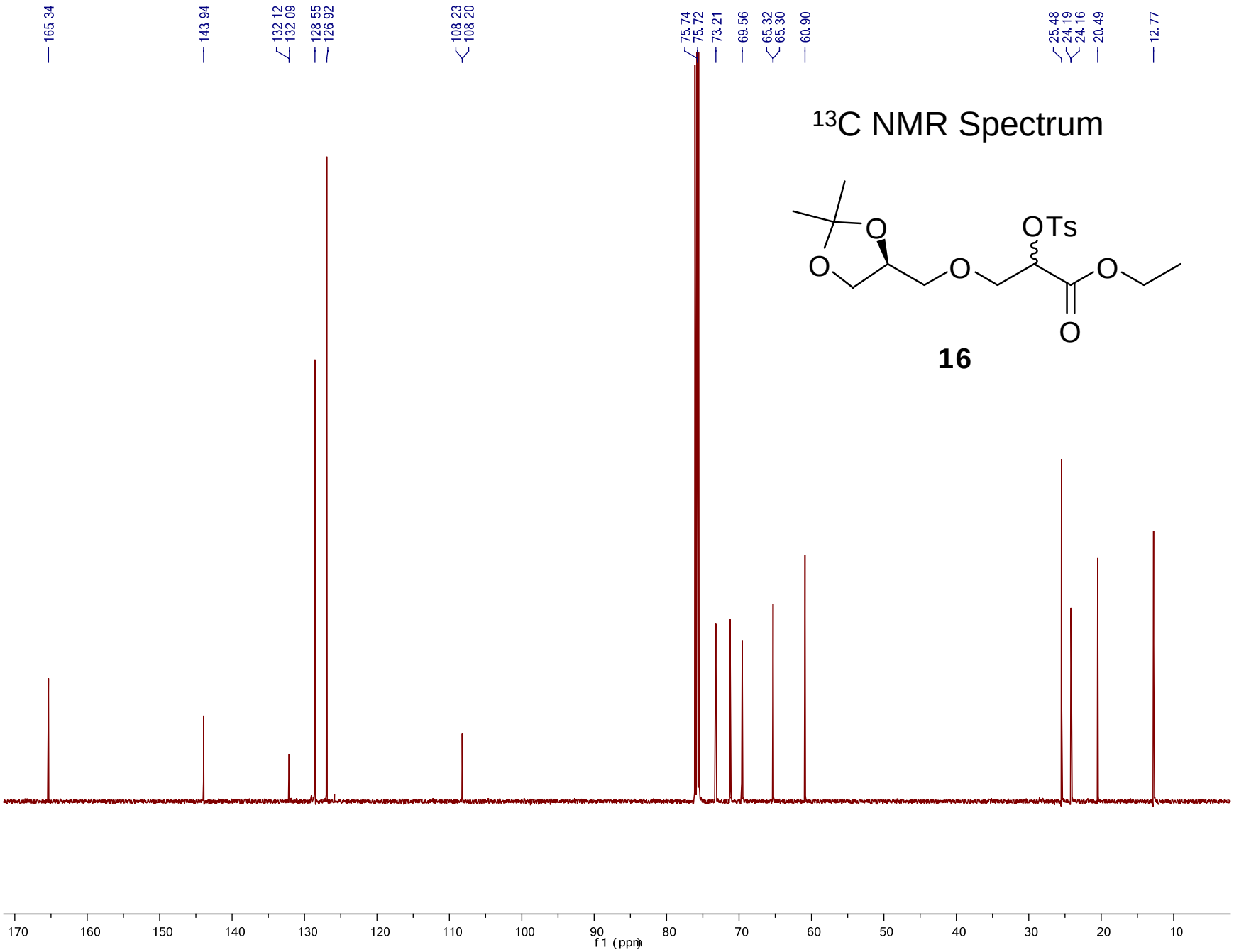

TOF Spectrum
TOF
Profile Spectrum at 8701.14 min (scan 1)
Baseline = 0
Abundance Min = 0
Abundance Max = 2087456
271.12222
519.2454
272.12069
520.24856
273.12224
Abundance
2.0M
1.8M
1.6M
1.4M
1.2M
1.0M
0.8M
0.6M
0.4M
0.2M
0.0
500
1000
1500
2000
2500
3000
m/z
OH
O
O
O
O
O
15

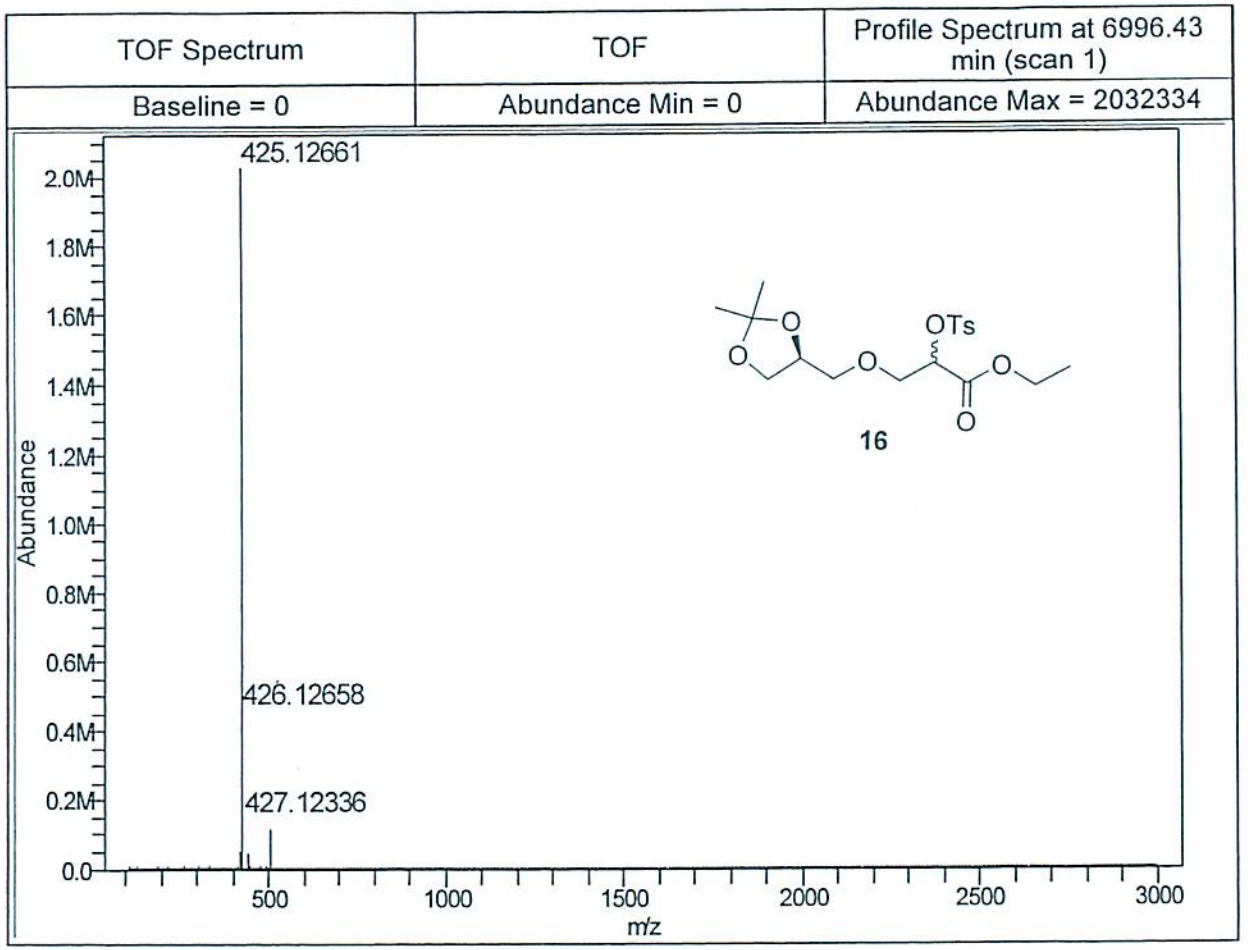
^{1}H NMR Spectrum



16

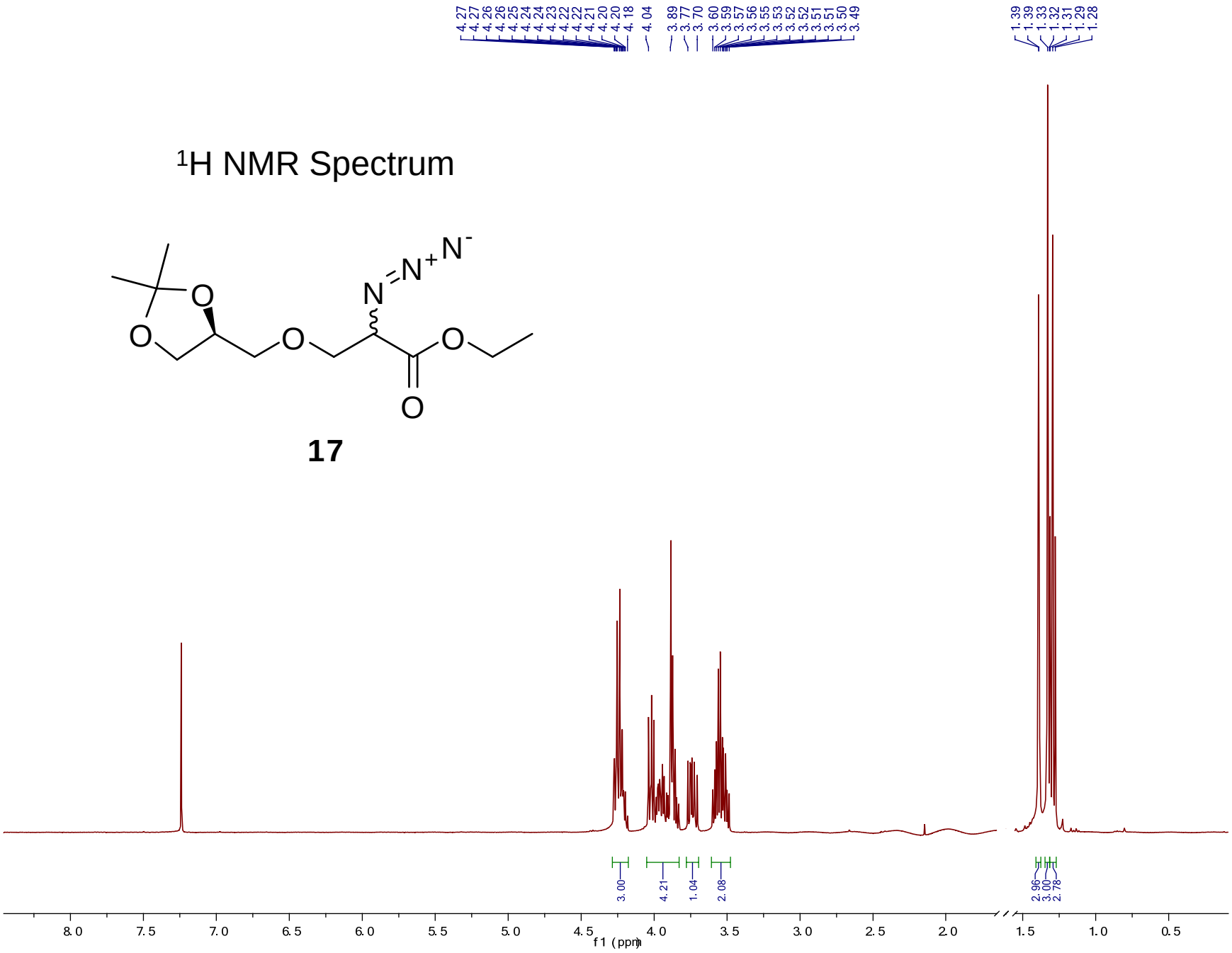


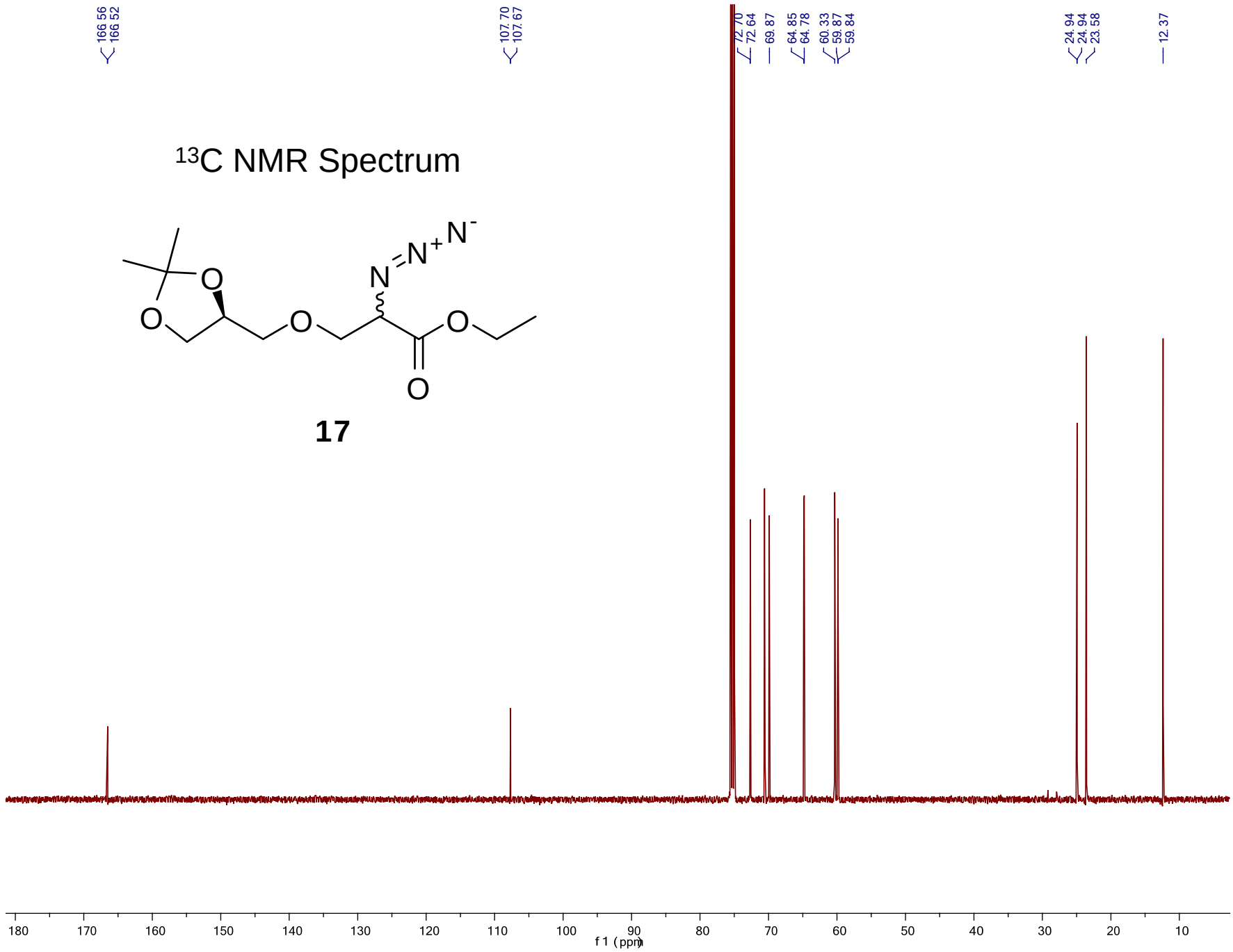

165.34
143.94
132.12
132.09
128.55
126.92
108.23
108.20
75.74
75.72
73.21
69.56
65.32
65.30
60.90
25.48
24.19
24.16
20.49
12.77
13C NMR Spectrum
OTs
O
O
O
O
O
16
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

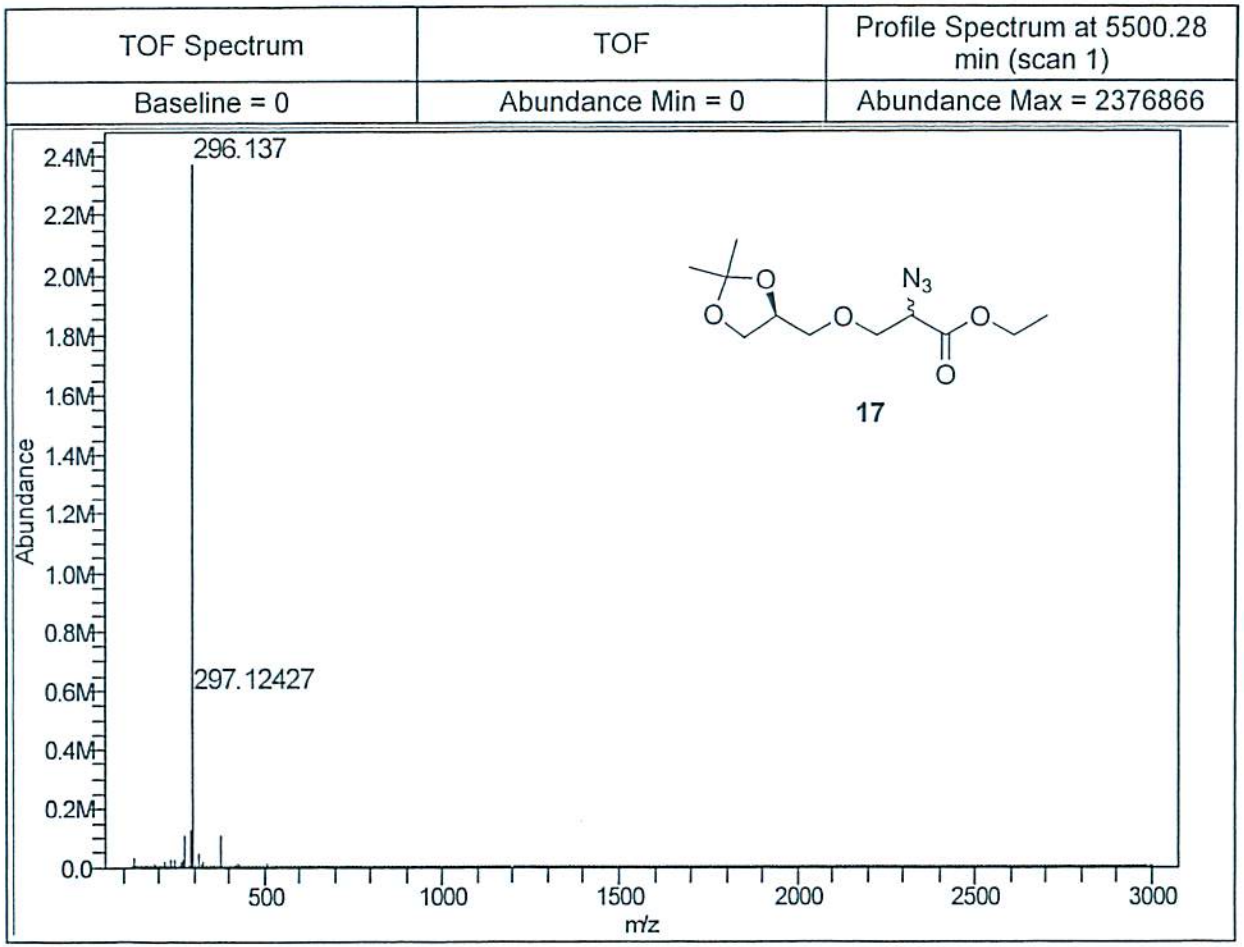

TOF Spectrum
TOF
Profile Spectrum at 6996.43 min (scan 1)
Baseline = 0
Abundance Min = 0
Abundance Max = 2032334
425.12661
426.12658
427.12336
Abundance
m/z
2.0M
1.8M
1.6M
1.4M
1.2M
1.0M
0.8M
0.6M
0.4M
0.2M
0.0
500
1000
1500
2000
2500
3000
OTs
16

^{1}H NMR Spectrum

17

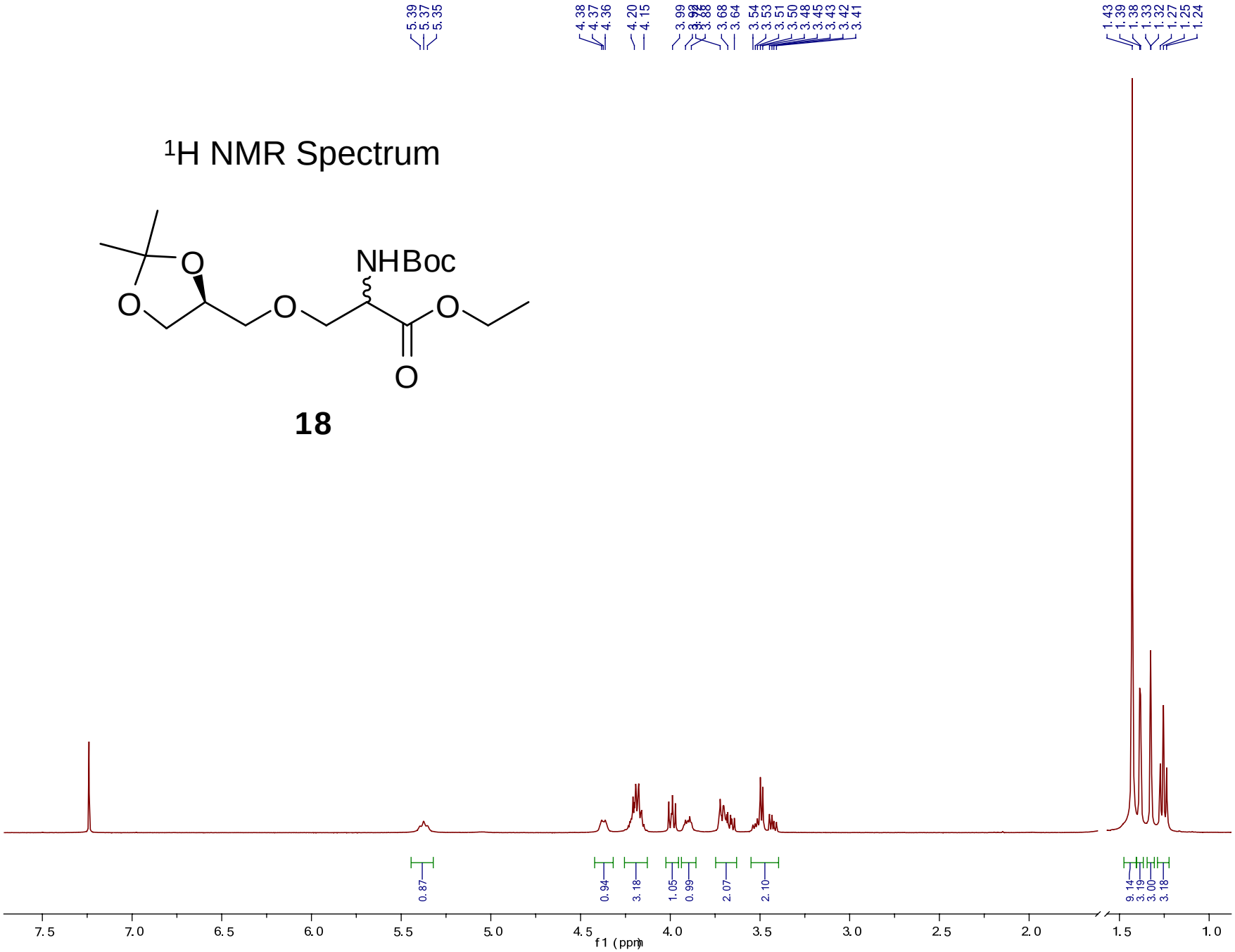


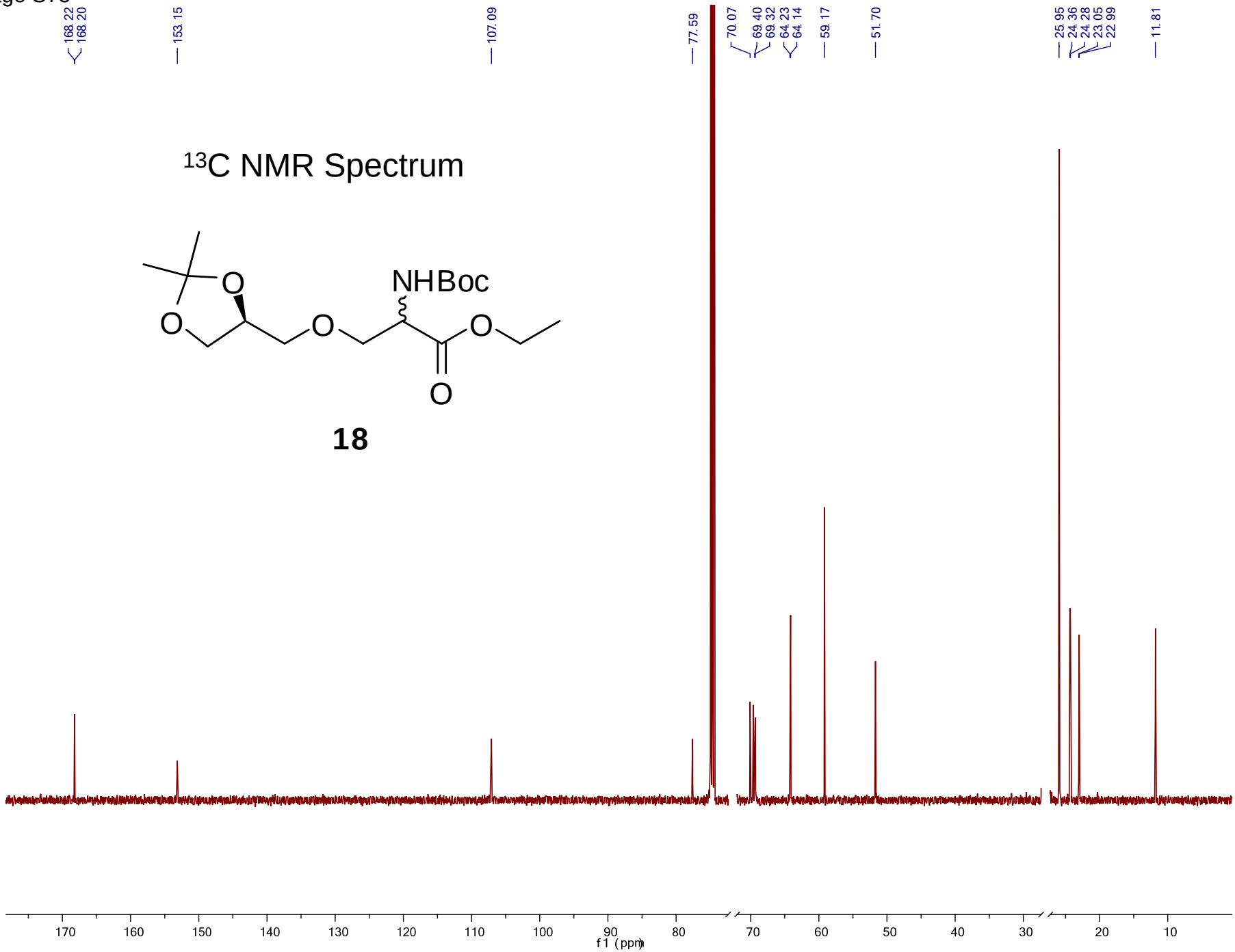

166.56
166.52
107.70
107.67
72.70
72.64
69.87
64.85
64.78
60.33
59.87
59.84
24.94
24.94
23.58
12.37
13C NMR Spectrum
O
O
O
N
N+
N-
O
17
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

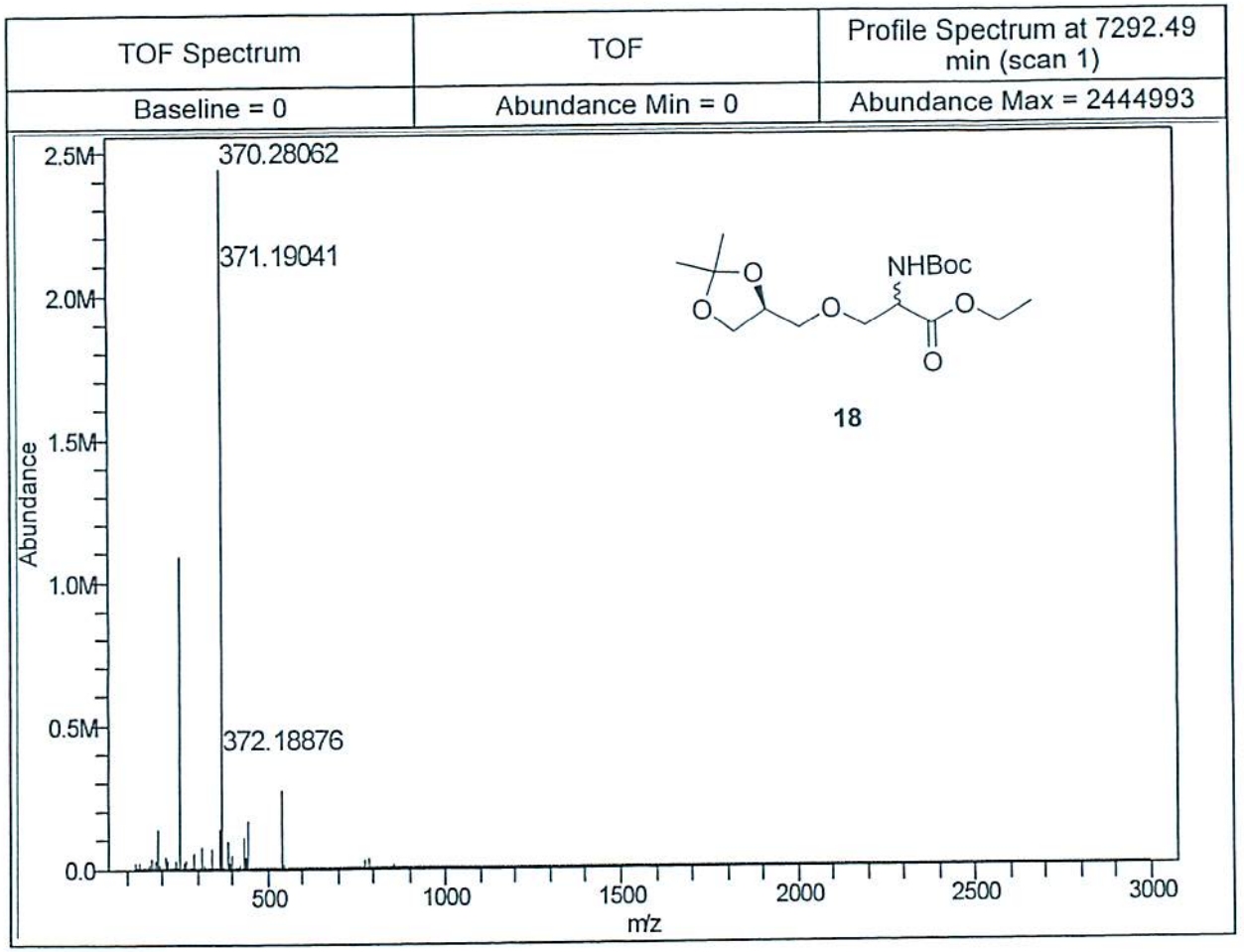

TOF Spectrum
TOF
Profile Spectrum at 5500.28 min (scan 1)
Baseline = 0
Abundance Min = 0
Abundance Max = 2376866
296.137
297.12427
Abundance
m/z
2.4M
2.2M
2.0M
1.8M
1.6M
1.4M
1.2M
1.0M
0.8M
0.6M
0.4M
0.2M
0.0
500
1000
1500
2000
2500
3000
N3
O
17

^{1}H NMR Spectrum

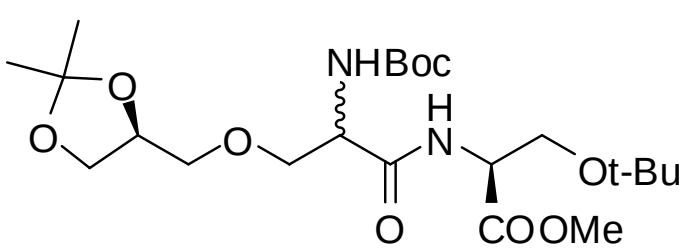
18



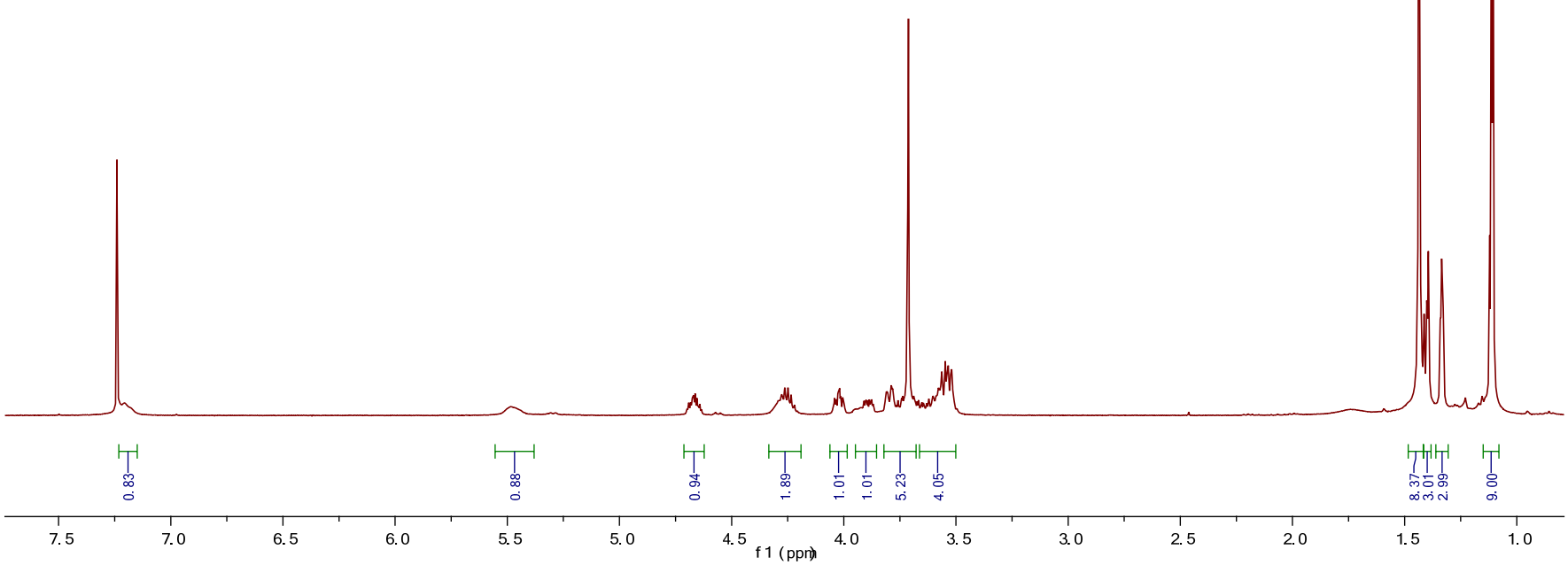

168.22
168.20
153.15
107.09
77.59
70.07
69.40
69.32
64.23
64.14
59.17
51.70
25.95
24.36
24.28
23.05
22.99
11.81
13C NMR Spectrum
NHBoc
O
O
O
O
O
18
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

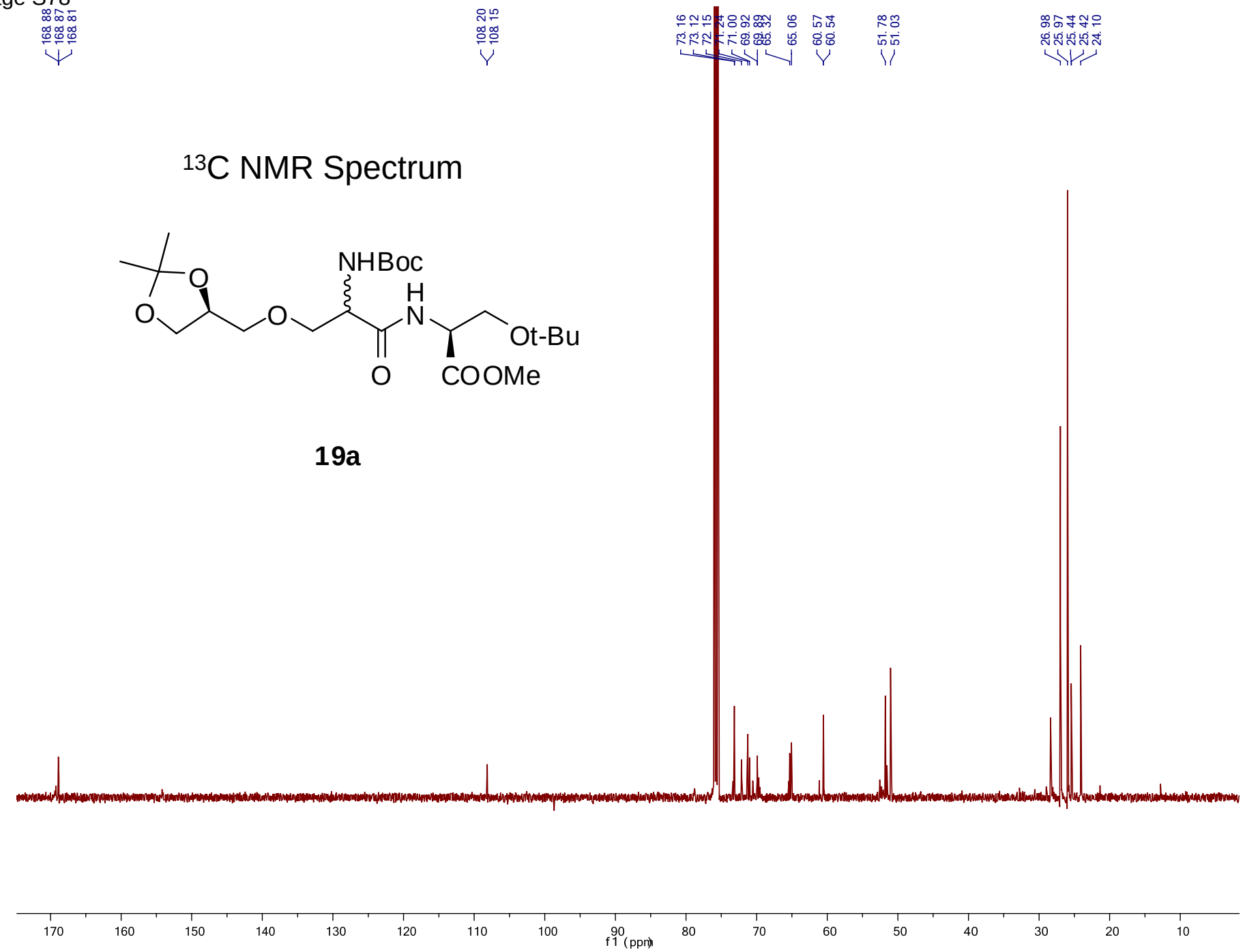

TOF Spectrum
TOF
Profile Spectrum at 7292.49 min (scan 1)
Baseline = 0
Abundance Min = 0
Abundance Max = 2444993
370.28062
371.19041
372.18876
2.5M
2.0M
1.5M
1.0M
0.5M
0.0
Abundance
500
1000
1500
2000
2500
3000
m/z
NHBoc
O
O
O
O
O
18

^{1}H NMR Spectrum



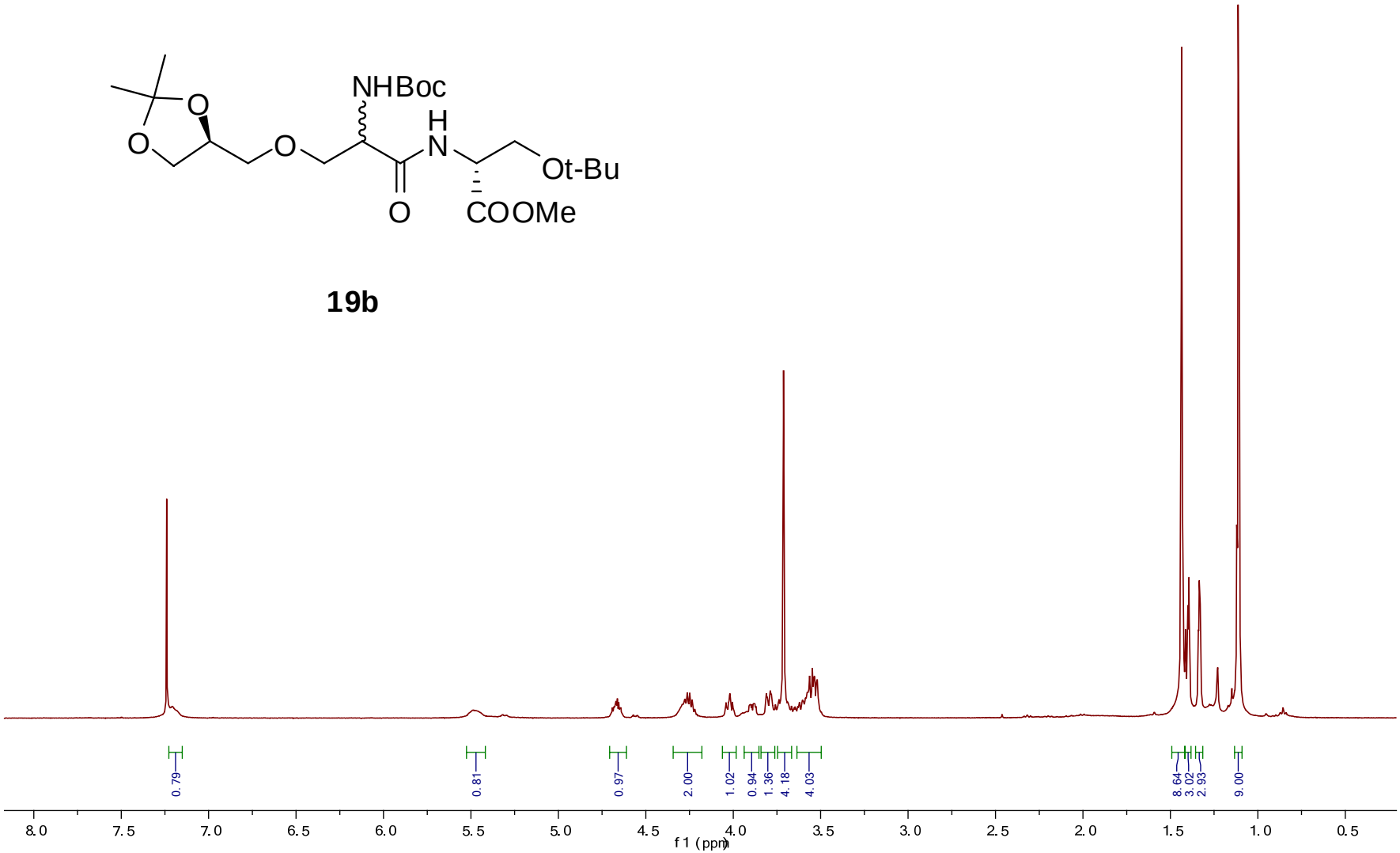
19a

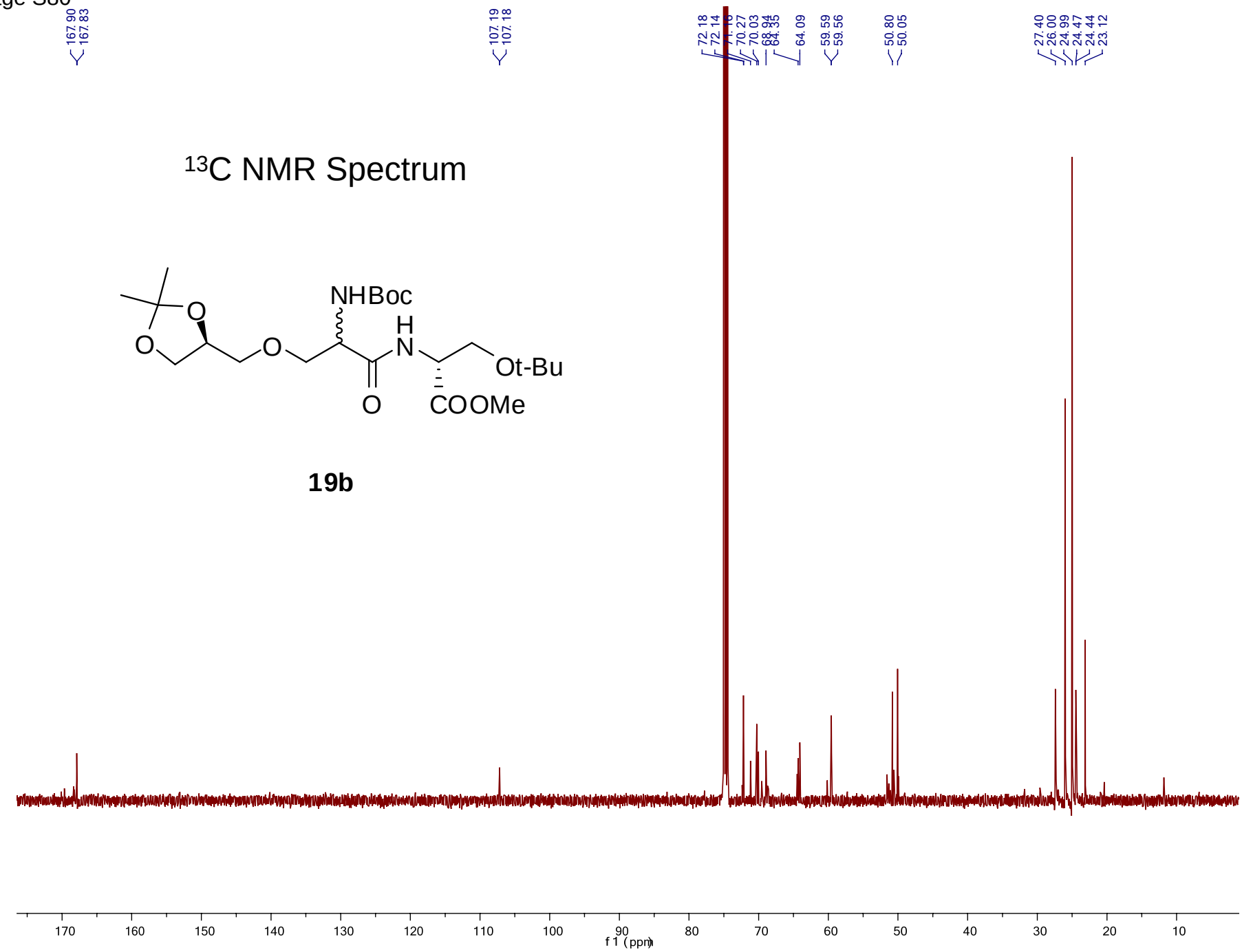


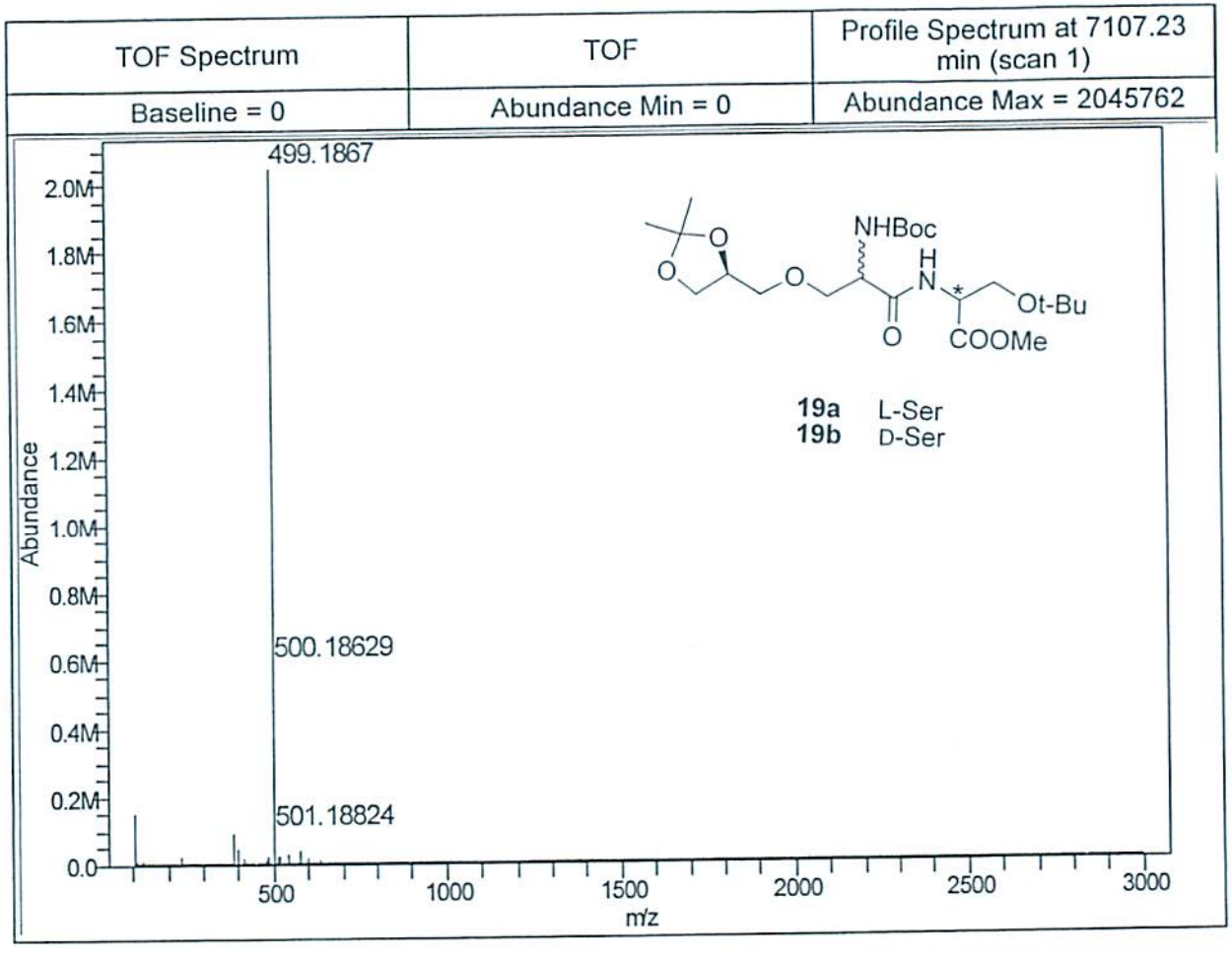

168.88
168.87
168.81
108.20
108.15
73.16
73.12
72.15
71.24
71.00
69.92
65.32
65.06
60.57
60.54
51.78
51.03
26.98
25.97
25.44
25.42
24.10
13C NMR Spectrum
NHBoc
H
N
O
O
O
O
Ot-Bu
CO OMe
19a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

^{1}H NMR Spectrum

19b

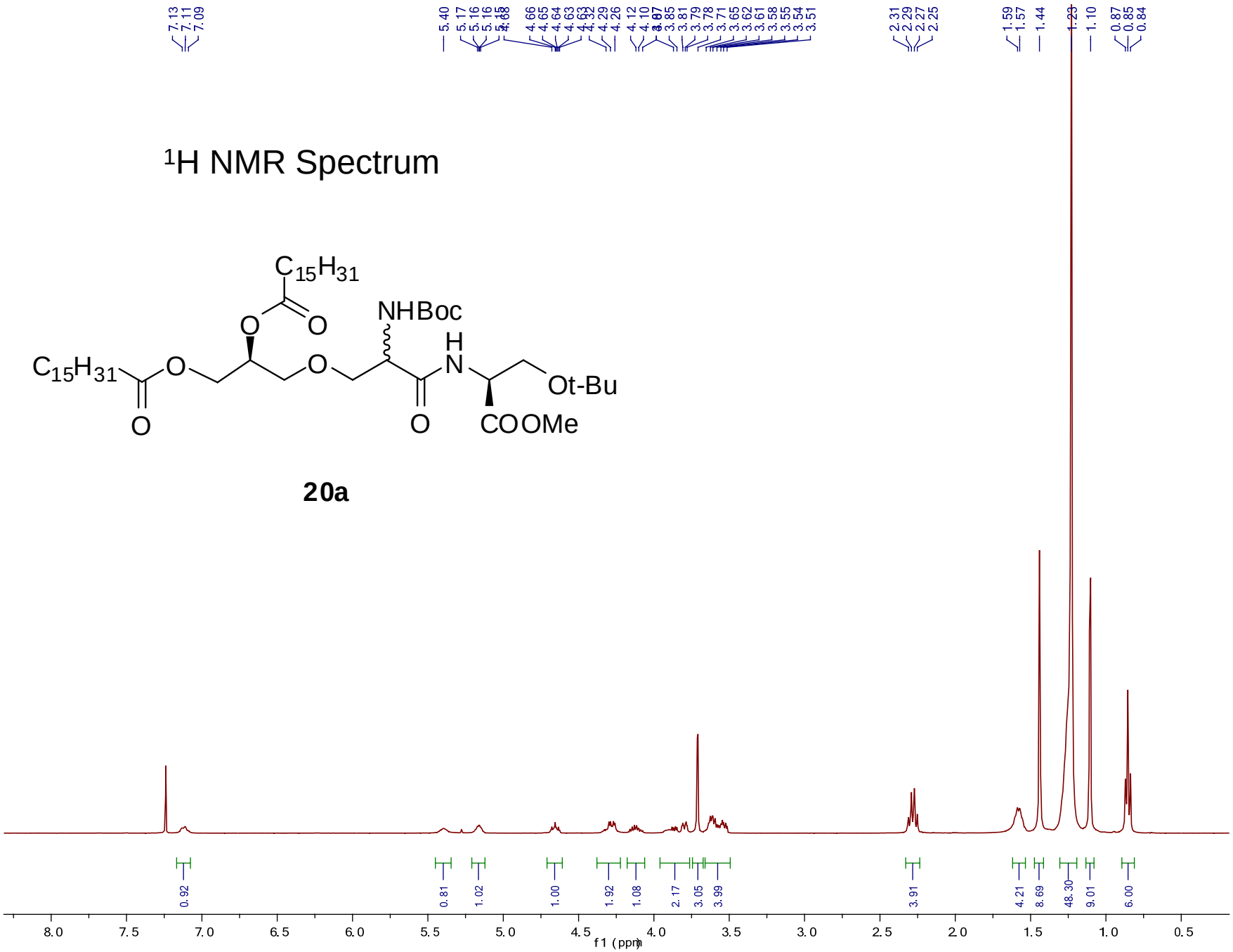


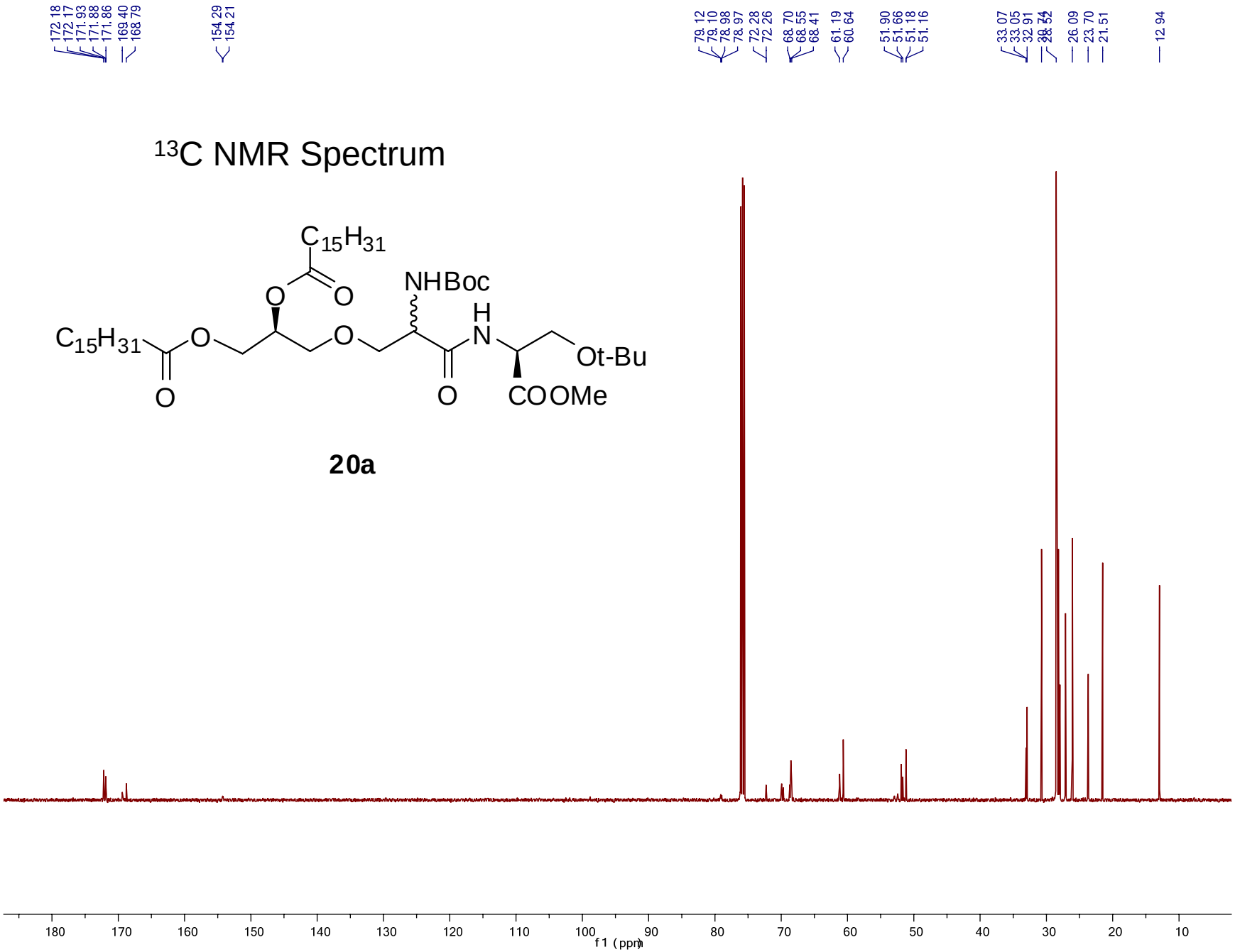

167.90
167.83
107.19
107.18
72.18
72.14
71.16
70.27
70.03
68.94
64.35
64.09
59.59
59.56
50.80
50.05
27.40
26.00
24.99
24.47
24.44
23.12
13C NMR Spectrum
NHBoc
H
N
O
O
O
O
Ot-Bu
CO OMe
19b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


TOF Spectrum
TOF
Profile Spectrum at 7107.23 min (scan 1)
Baseline = 0
Abundance Min = 0
Abundance Max = 2045762
499.1867
500.18629
501.18824
Abundance
2.0M
1.8M
1.6M
1.4M
1.2M
1.0M
0.8M
0.6M
0.4M
0.2M
0.0
500
1000
1500
2000
2500
3000
m/z
NHBoc
Ot-Bu
COOMe
19a L-Ser
19b D-Ser

^{1}H NMR Spectrum

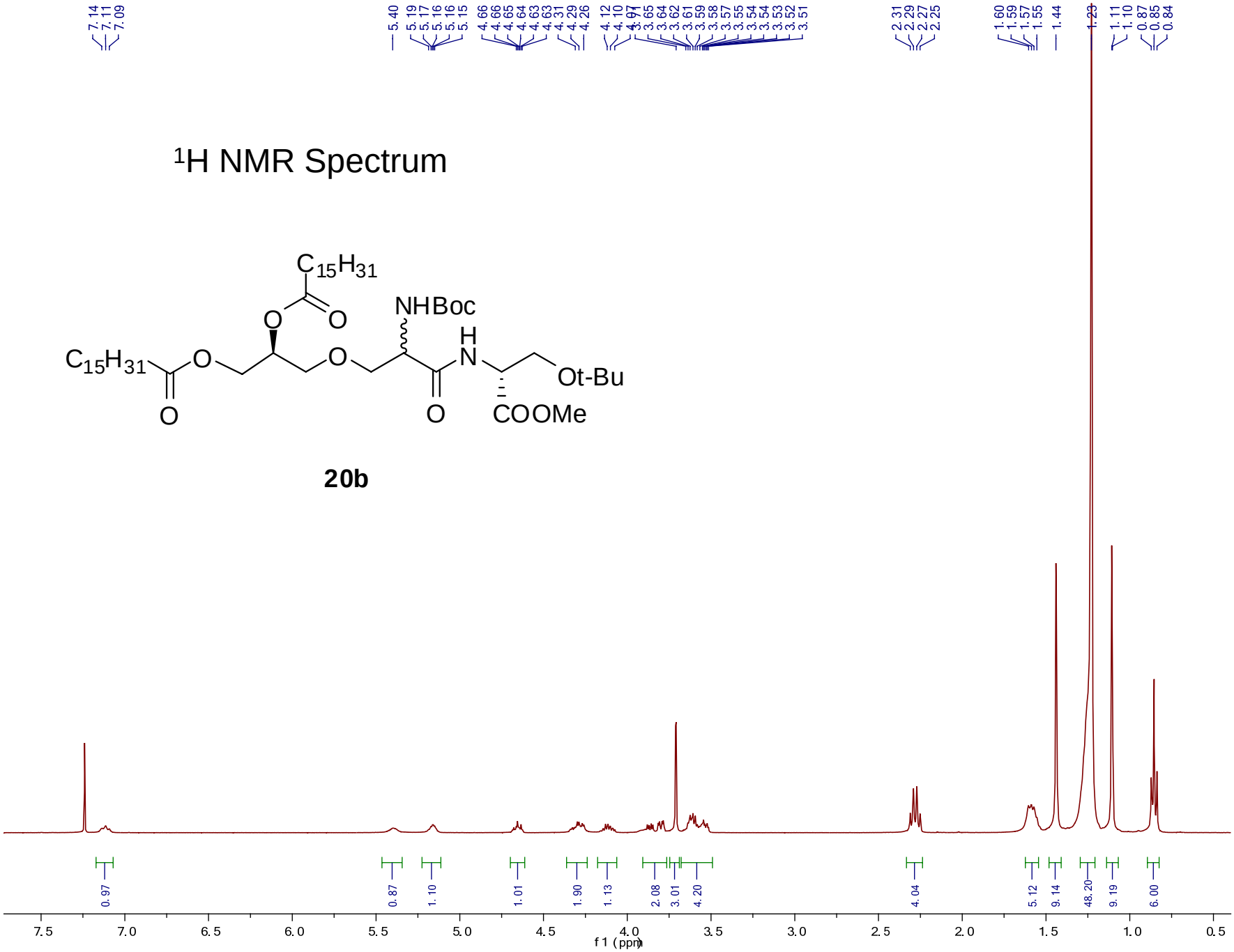
20a

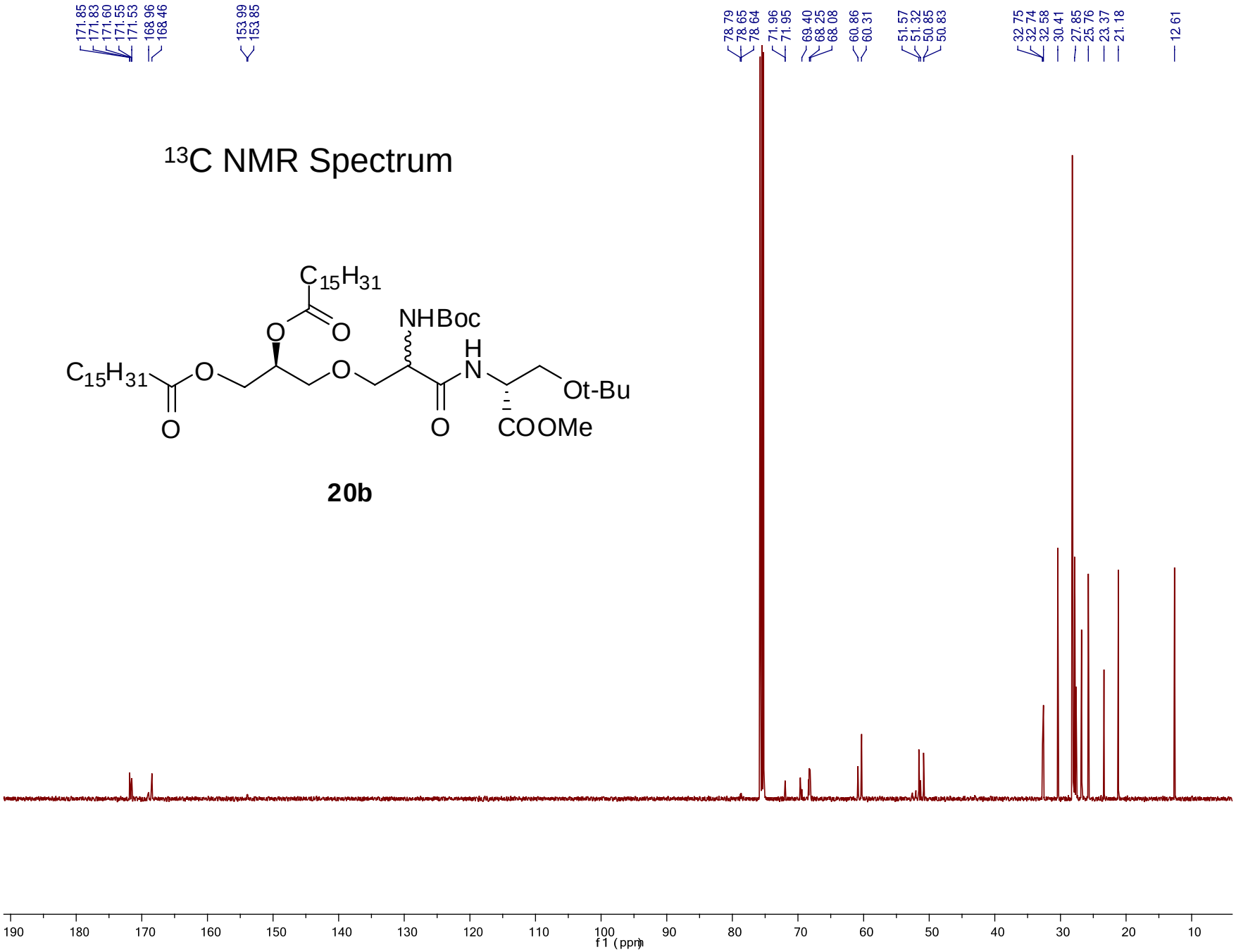


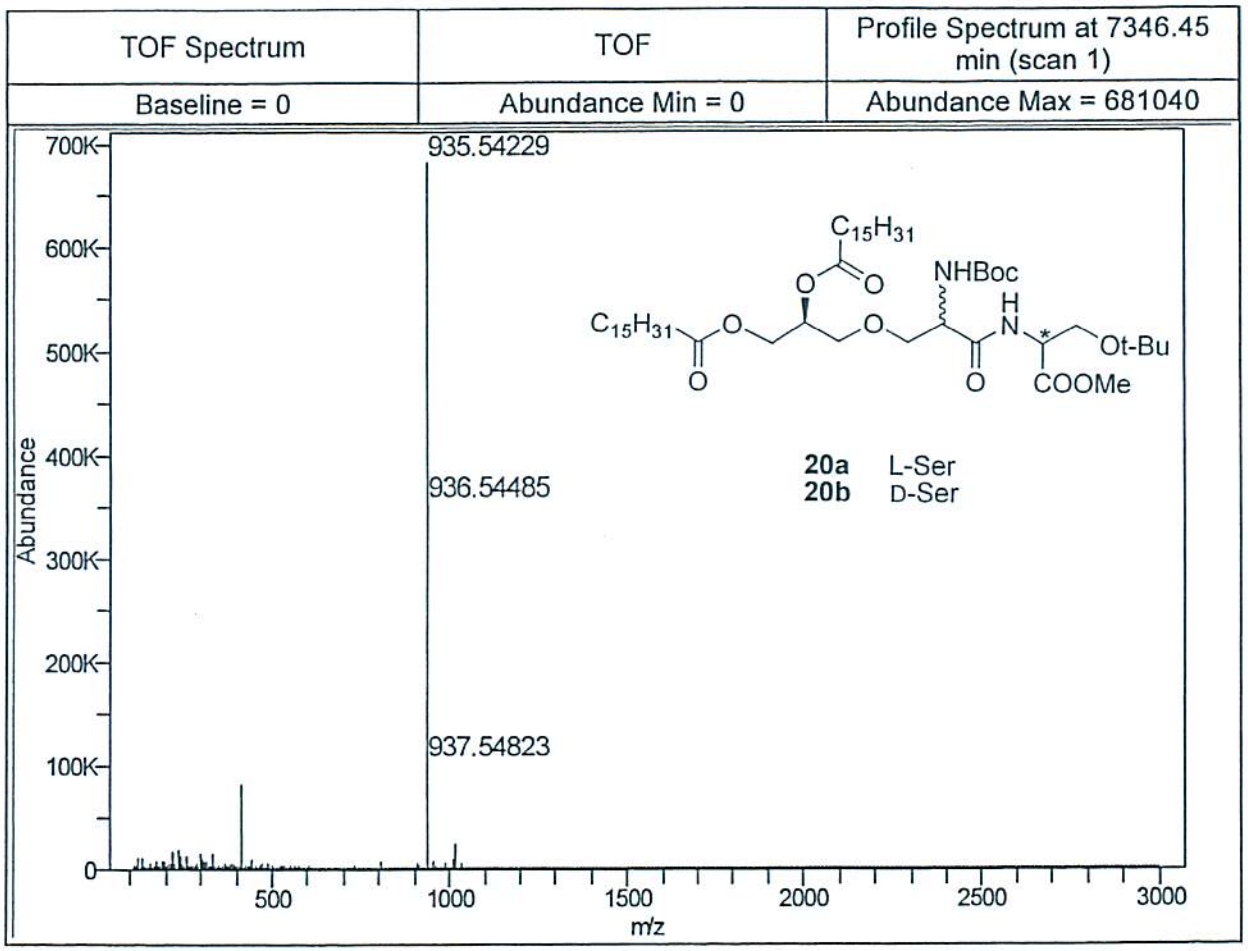

172.18
172.17
171.93
171.88
171.86
169.40
168.79
154.29
154.21
79.12
79.10
78.98
78.97
72.28
72.26
68.70
68.55
68.41
61.19
60.64
51.90
51.66
51.18
51.16
33.07
33.05
32.91
26.09
23.70
21.51
12.94
13C NMR Spectrum
C15H31
O
O
NHBoc
H
N
C15H31
O
O
O
Ot-Bu
O
CO OMe
20a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

^{1}H NMR Spectrum

20b

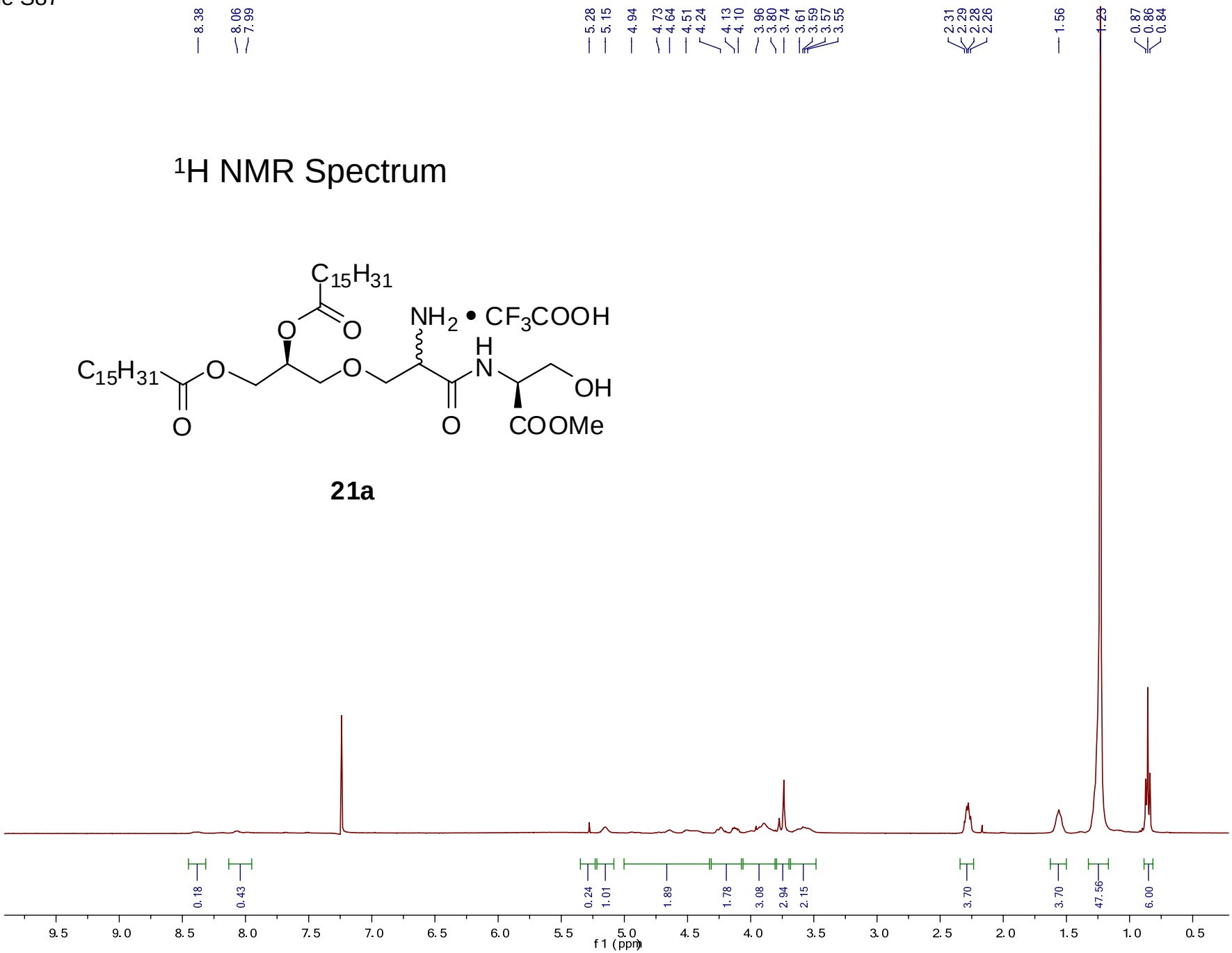



171.85
171.83
171.60
171.55
171.53
168.96
168.46
153.99
153.85
78.79
78.65
78.64
71.96
71.95
69.40
68.25
68.08
60.86
60.31
51.57
51.32
50.85
50.83
32.75
32.74
32.58
30.41
27.85
25.76
23.37
21.18
12.61
13C NMR Spectrum
C15H31
O
O
NHBoc
H
N
C15H31
O
O
O
Ot-Bu
O
COOMe
20b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


TOF Spectrum
TOF
Profile Spectrum at 7346.45 min (scan 1)
Baseline = 0
Abundance Min = 0
Abundance Max = 681040
935.54229
936.54485
937.54823
Abundance
m/z
700K
600K
500K
400K
300K
200K
100K
0
500
1000
1500
2000
2500
3000
C15H31
NHBoc
Ot-Bu
COOMe
20a L-Ser
20b D-Ser

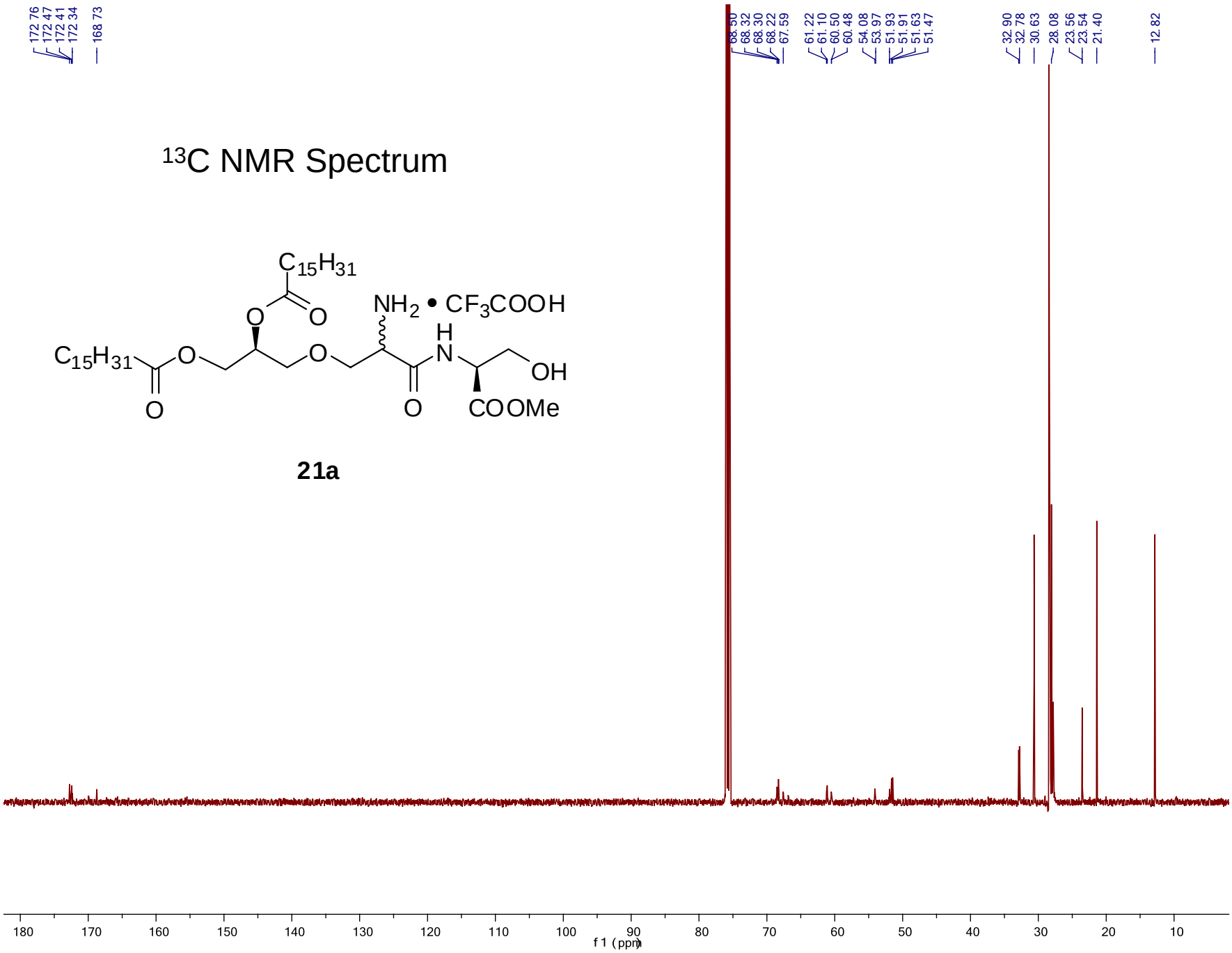
^{1}H NMR Spectrum

21a



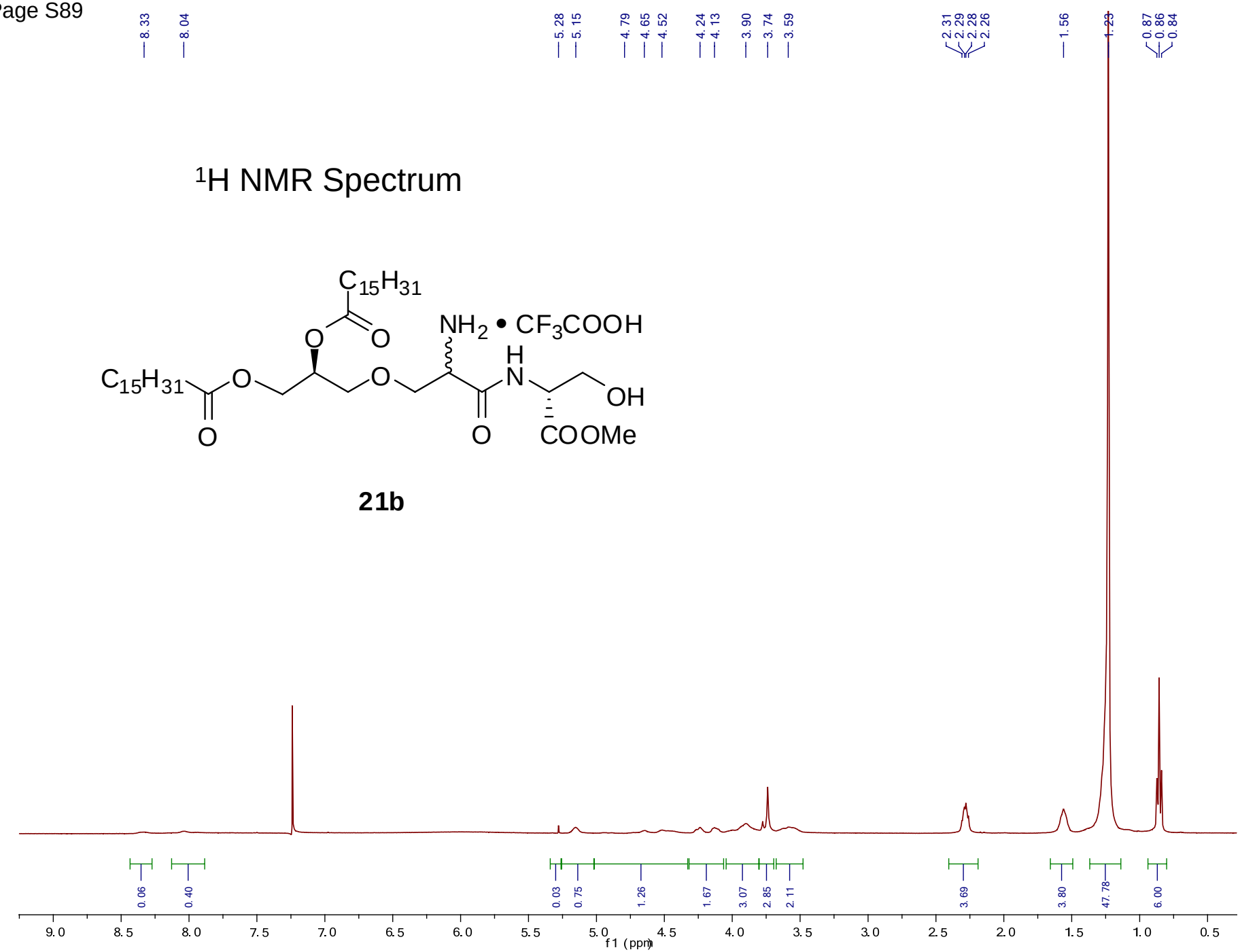
^{13}C NMR Spectrum

21a



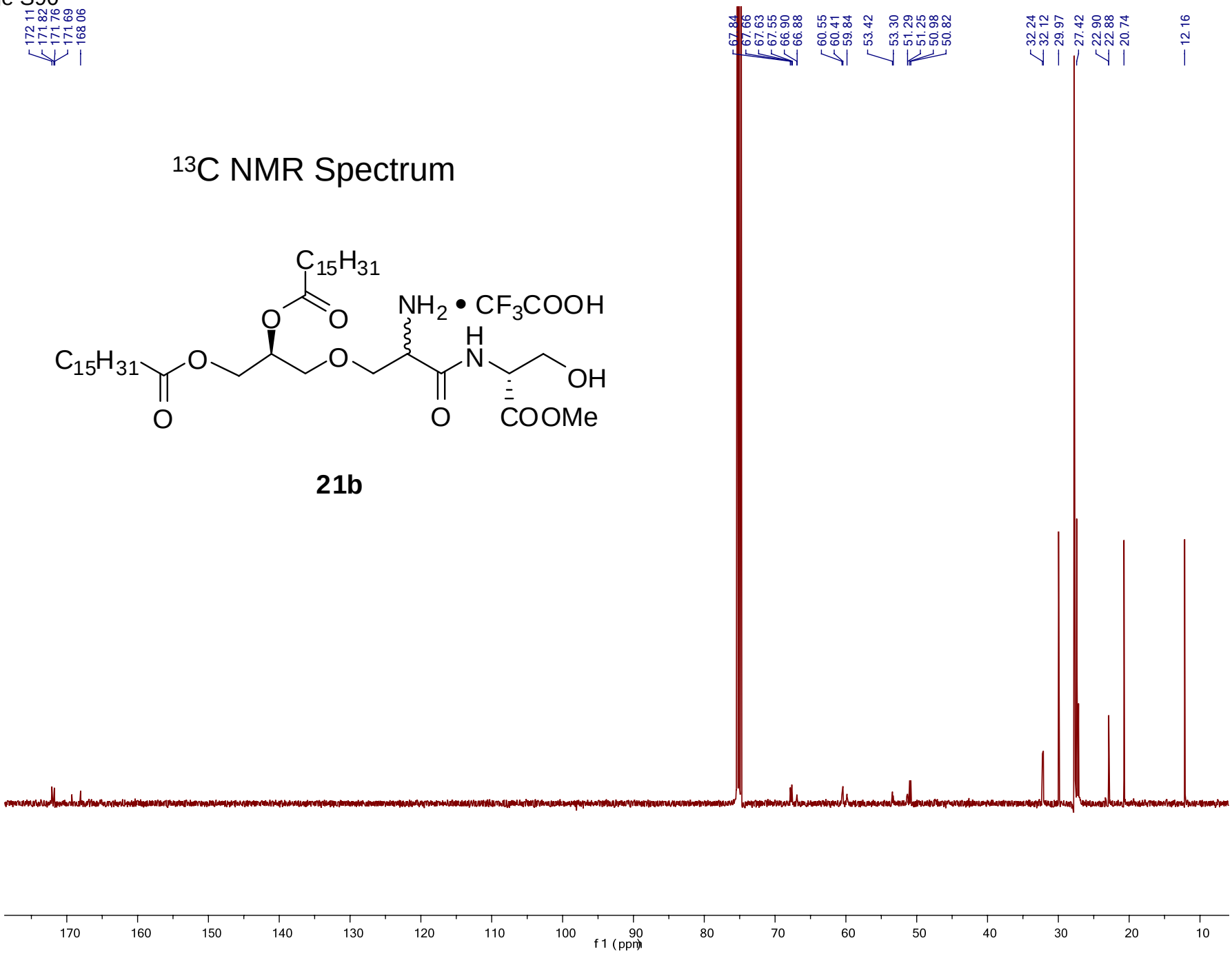
^{1}H NMR Spectrum

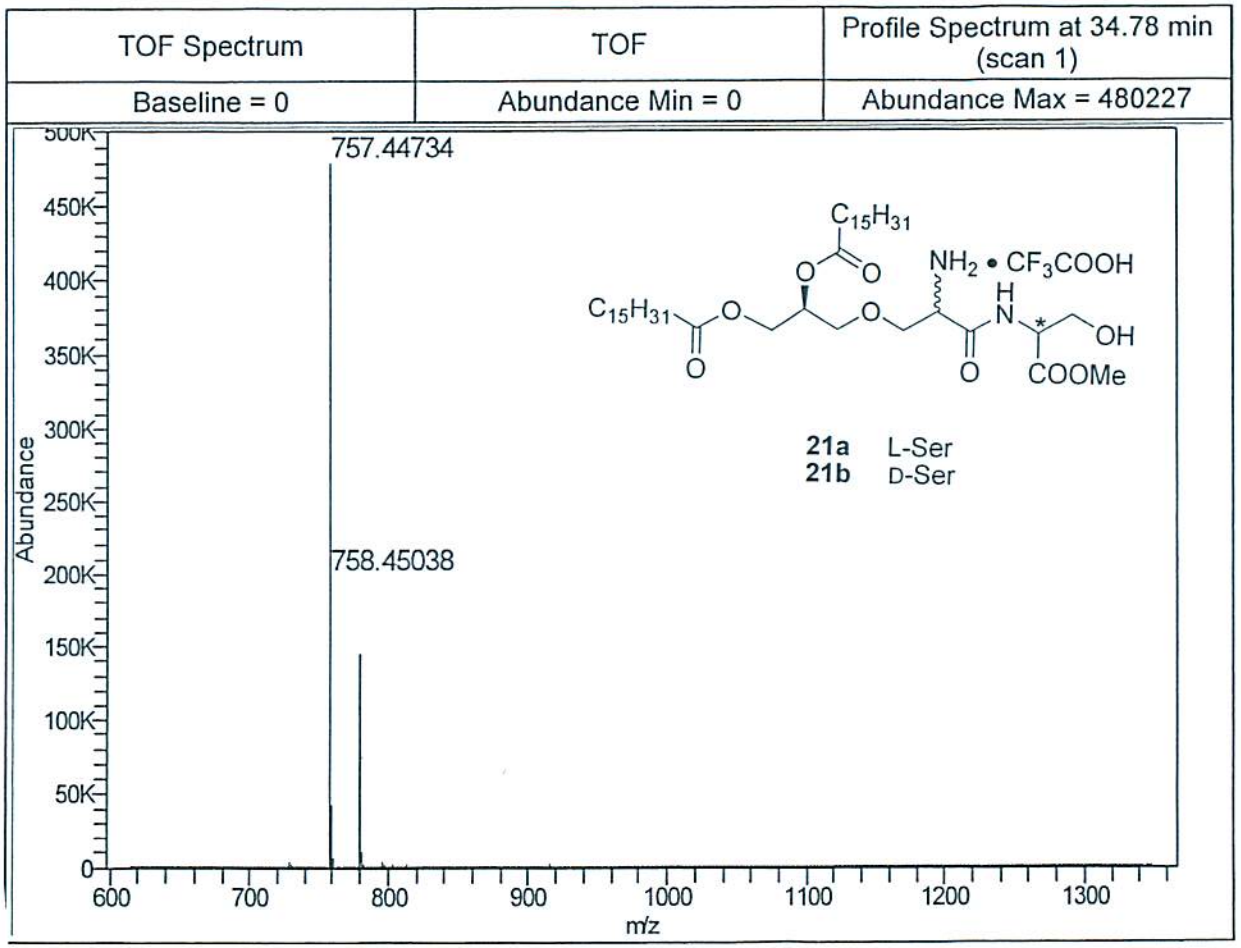
21b

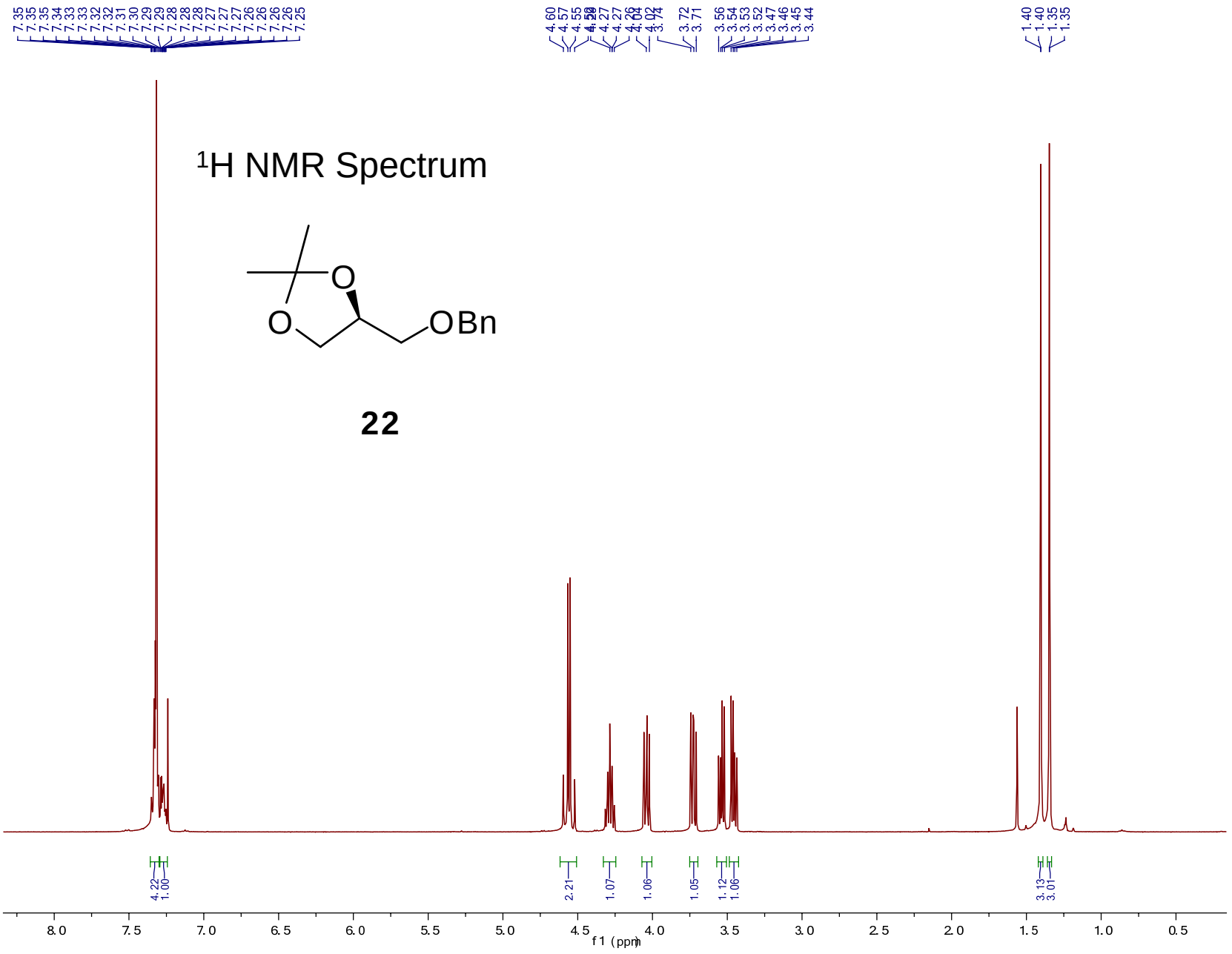


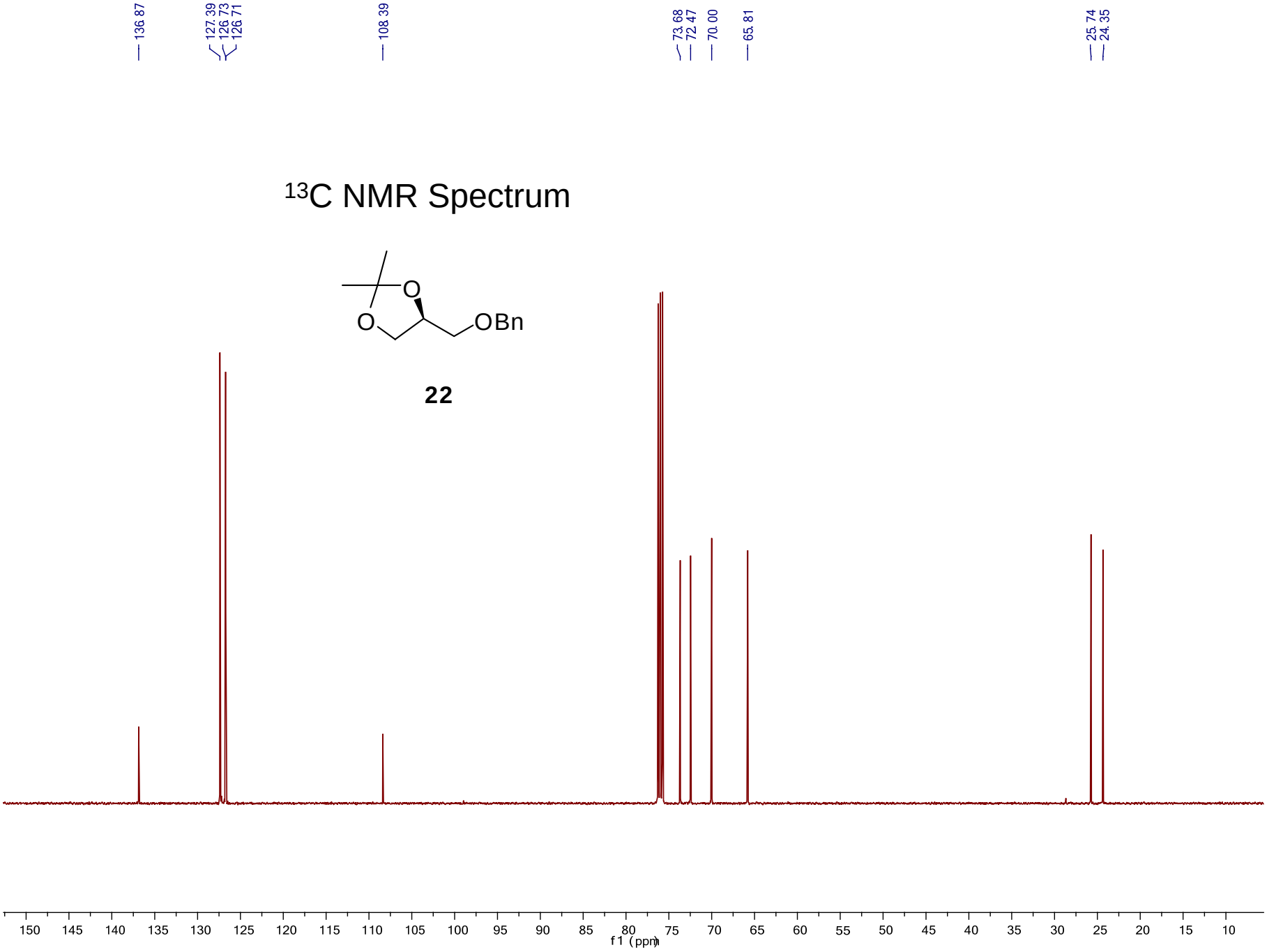
^{13}C NMR Spectrum

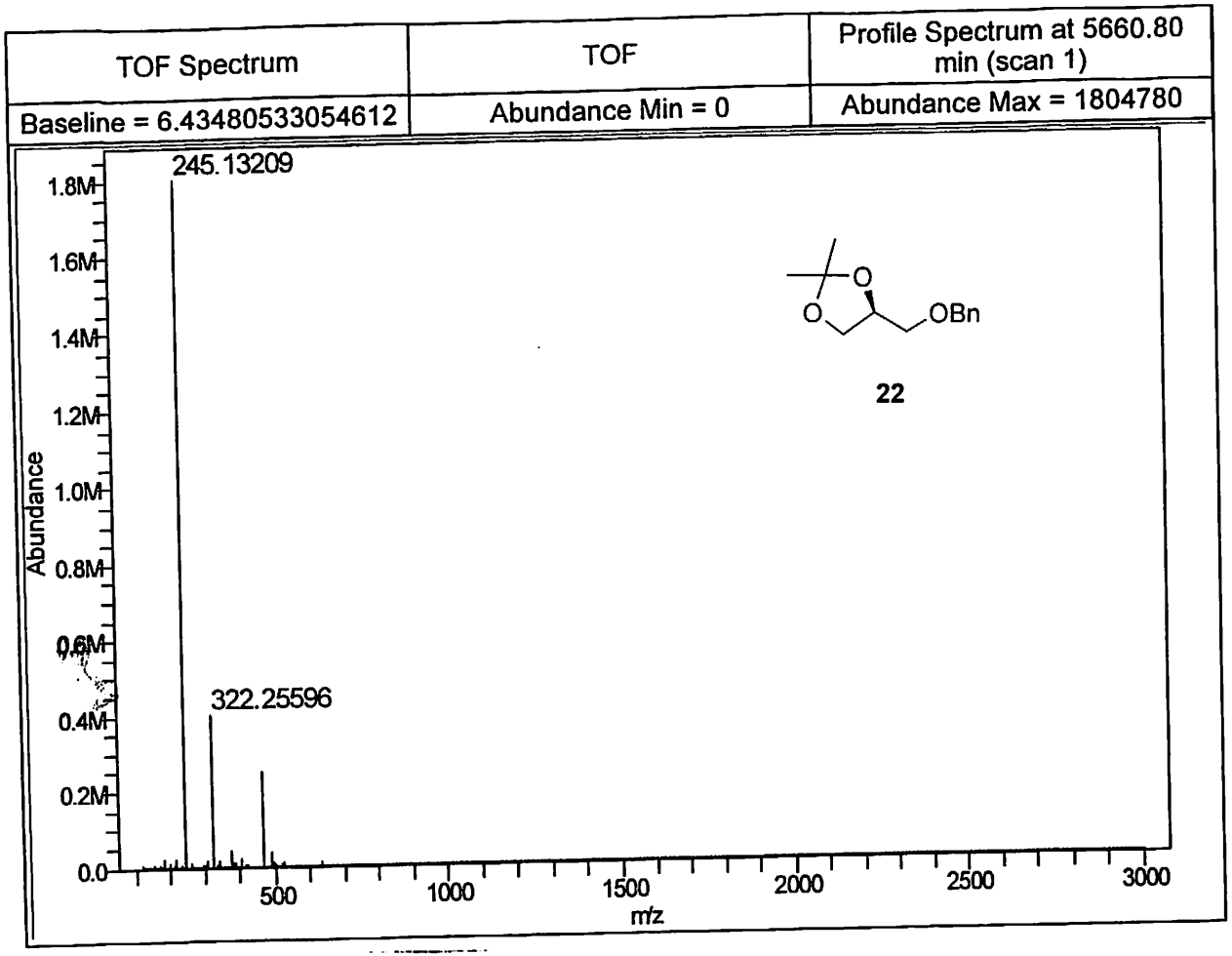
21b

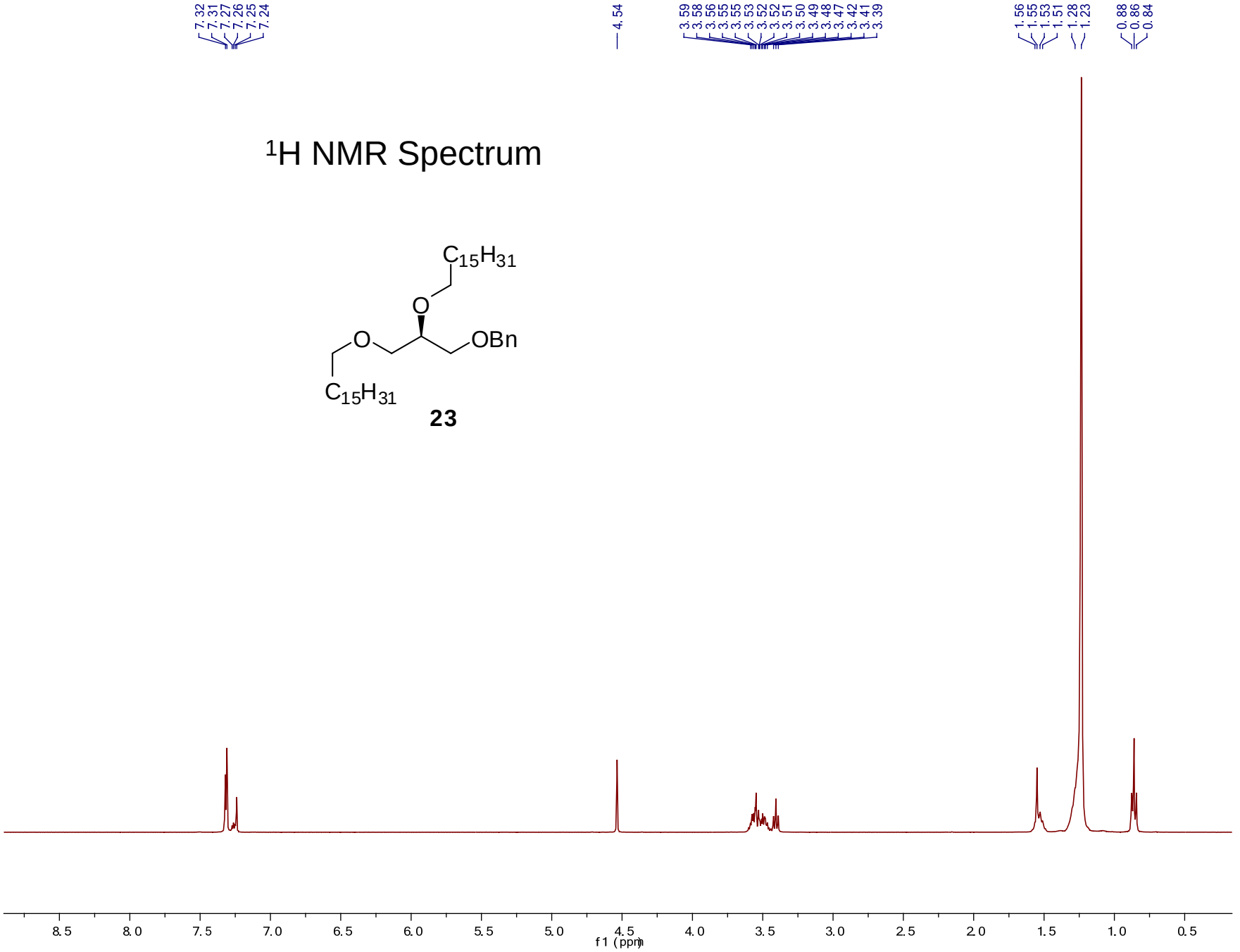



TOF Spectrum
TOF
Profile Spectrum at 34.78 min (scan 1)
Baseline = 0
Abundance Min = 0
Abundance Max = 480227
757.44734
758.45038
Abundance
m/z
500K
450K
400K
350K
300K
250K
200K
150K
100K
50K
0
600
700
800
900
1000
1100
1200
1300
C15H31
NH2 • CF3COOH
OH
COOMe
21a L-Ser
21b D-Ser


1H NMR Spectrum
O
O
OBn
22
f1 (ppm)

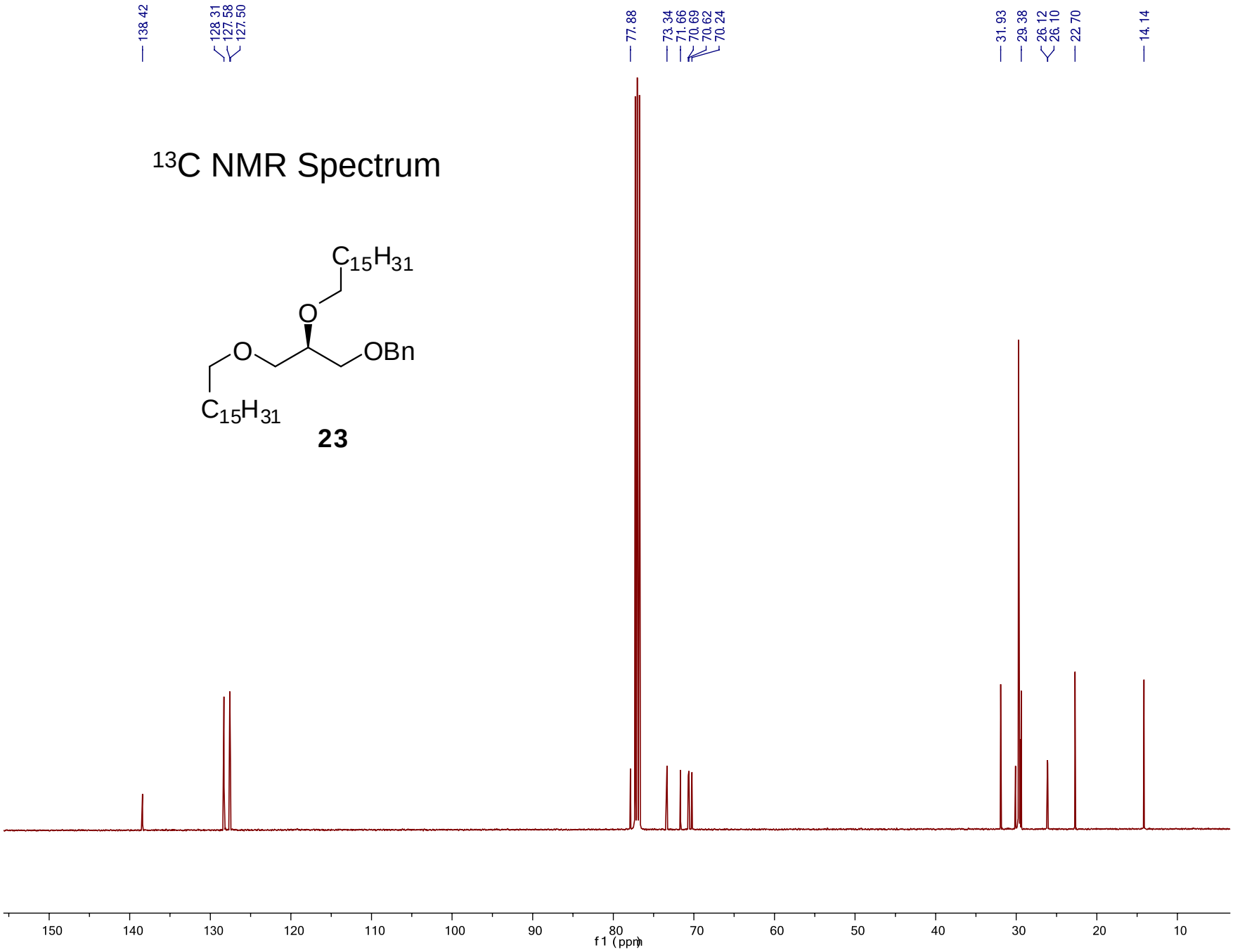

136.87
127.39
126.73
126.71
108.39
73.68
72.47
70.00
65.81
25.74
24.35
13C NMR Spectrum
O
O
OBn
22
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)

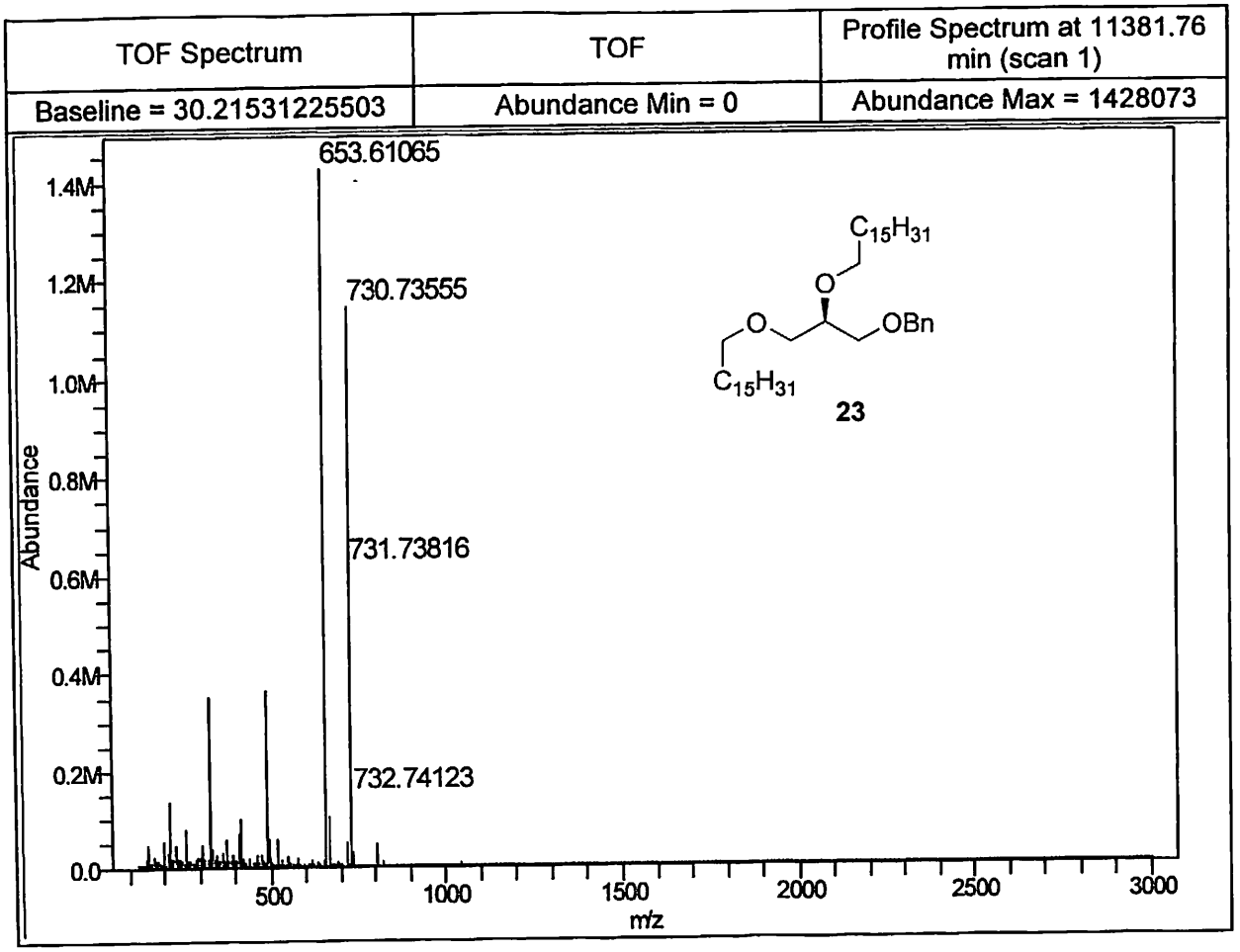

TOF Spectrum
TOF
Profile Spectrum at 5660.80 min (scan 1)
Baseline = 6.43480533054612
Abundance Min = 0
Abundance Max = 1804780
245.13209
322.25596
Abundance
1.8M
1.6M
1.4M
1.2M
1.0M
0.8M
0.6M
0.4M
0.2M
0.0
500
1000
1500
2000
2500
3000
m/z
O
O
OBn
22



^{1}H NMR Spectrum

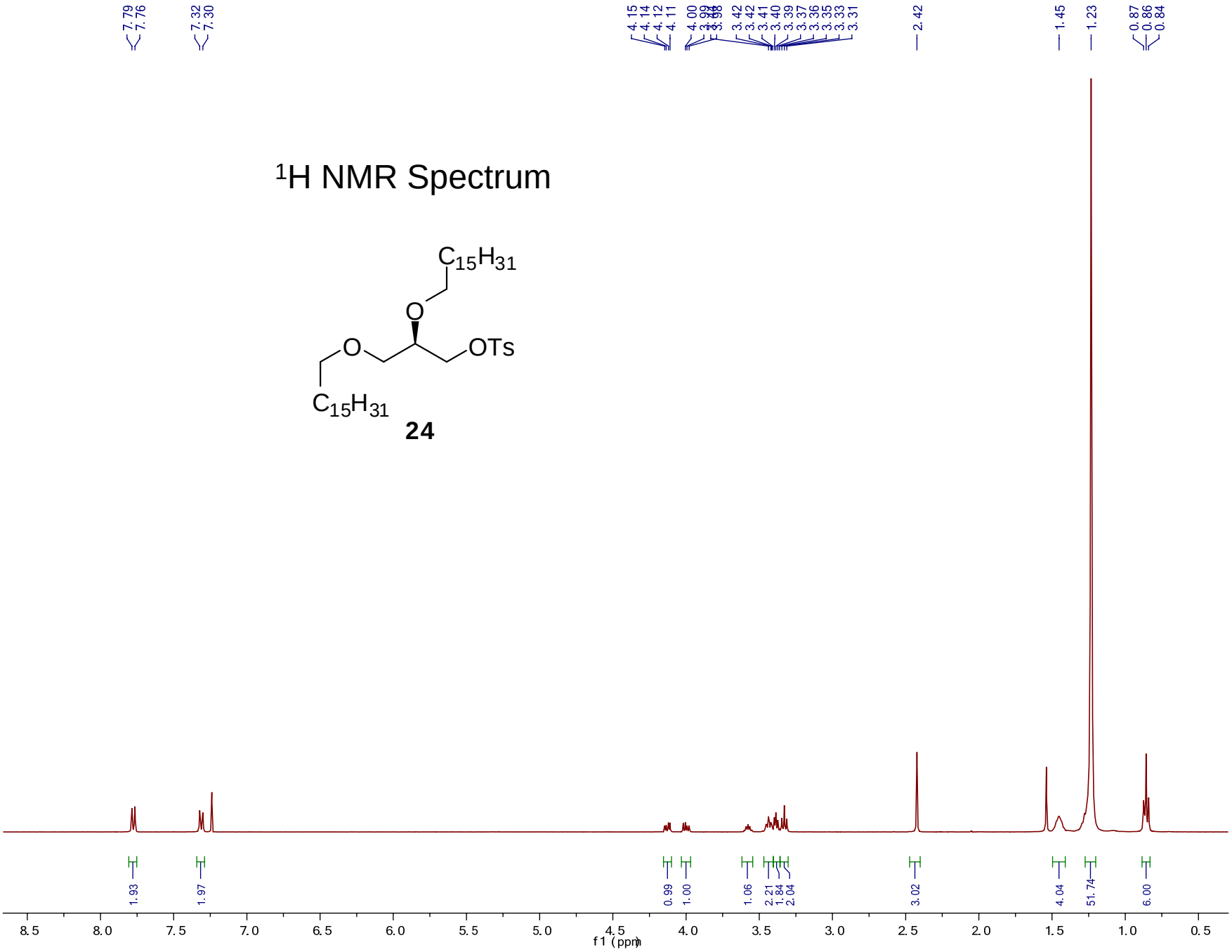
23

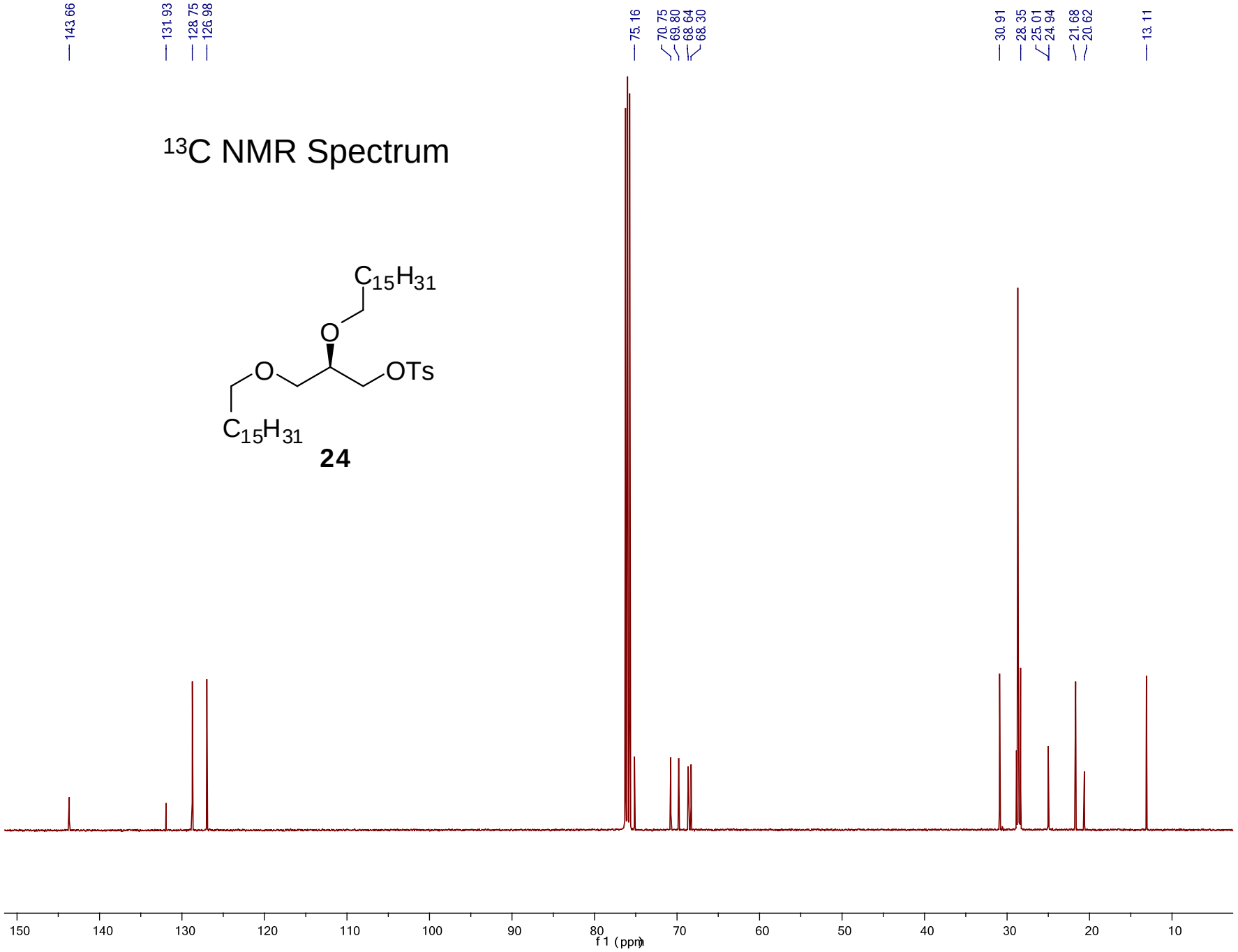

138.42
128.31
127.58
127.50
77.88
73.34
71.66
70.69
70.62
70.24
31.93
29.38
26.12
26.10
22.70
14.14
13C NMR Spectrum
C15H31
O
O
OBn
C15H31
23
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

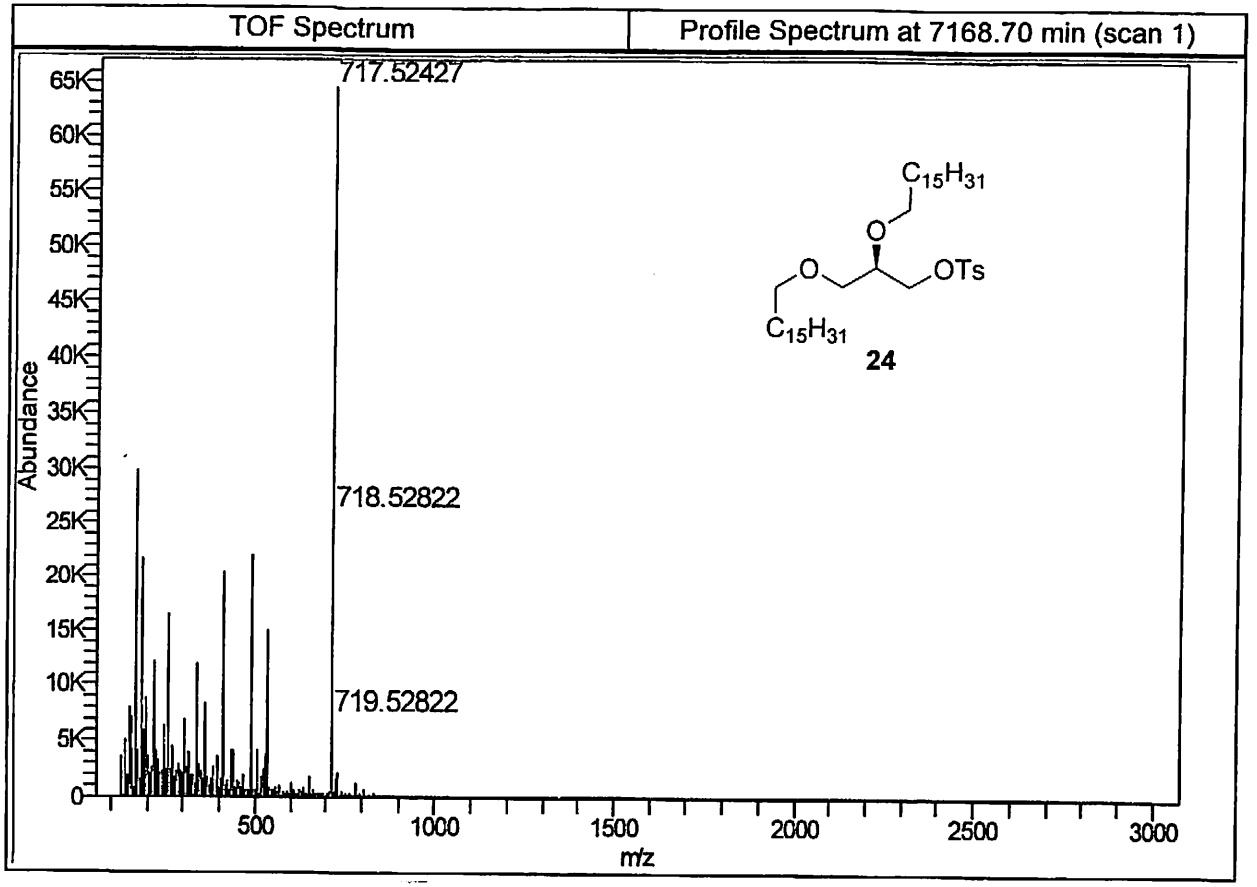

TOF Spectrum
TOF
Profile Spectrum at 11381.76 min (scan 1)
Baseline = 30.21531225503
Abundance Min = 0
Abundance Max = 1428073
653.61065
730.73555
731.73816
732.74123
Abundance
1.4M
1.2M
1.0M
0.8M
0.6M
0.4M
0.2M
0.0
500
1000
1500
2000
2500
3000
m/z
C15H31
O
O
OBn
C15H31
23

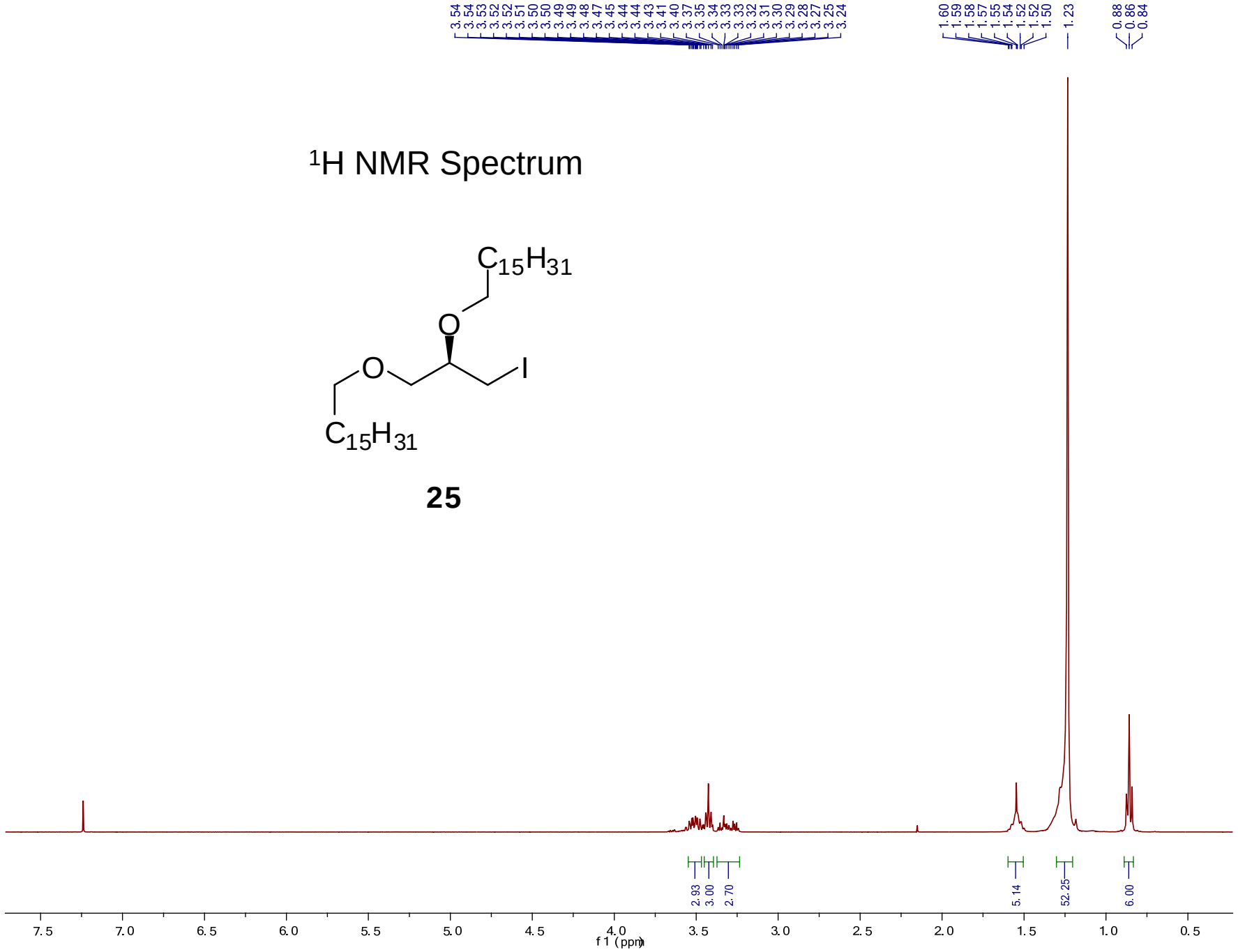
^{1}H NMR Spectrum

24



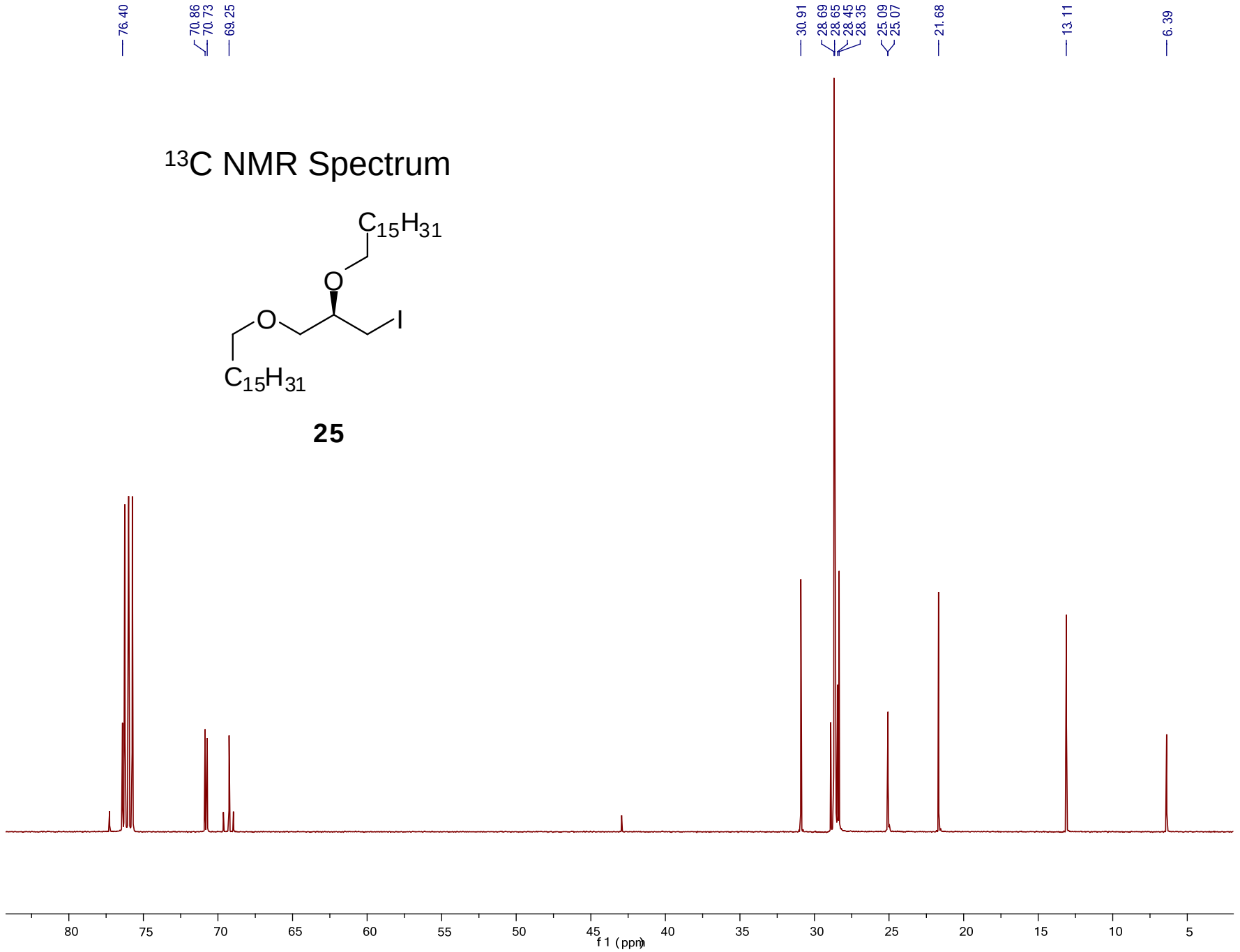

143.66
131.93
128.75
126.98
75.16
70.75
69.80
68.64
68.30
30.91
28.35
25.01
24.94
21.68
20.62
13.11
13C NMR Spectrum
C15H31
O
O
OTs
C15H31
24
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

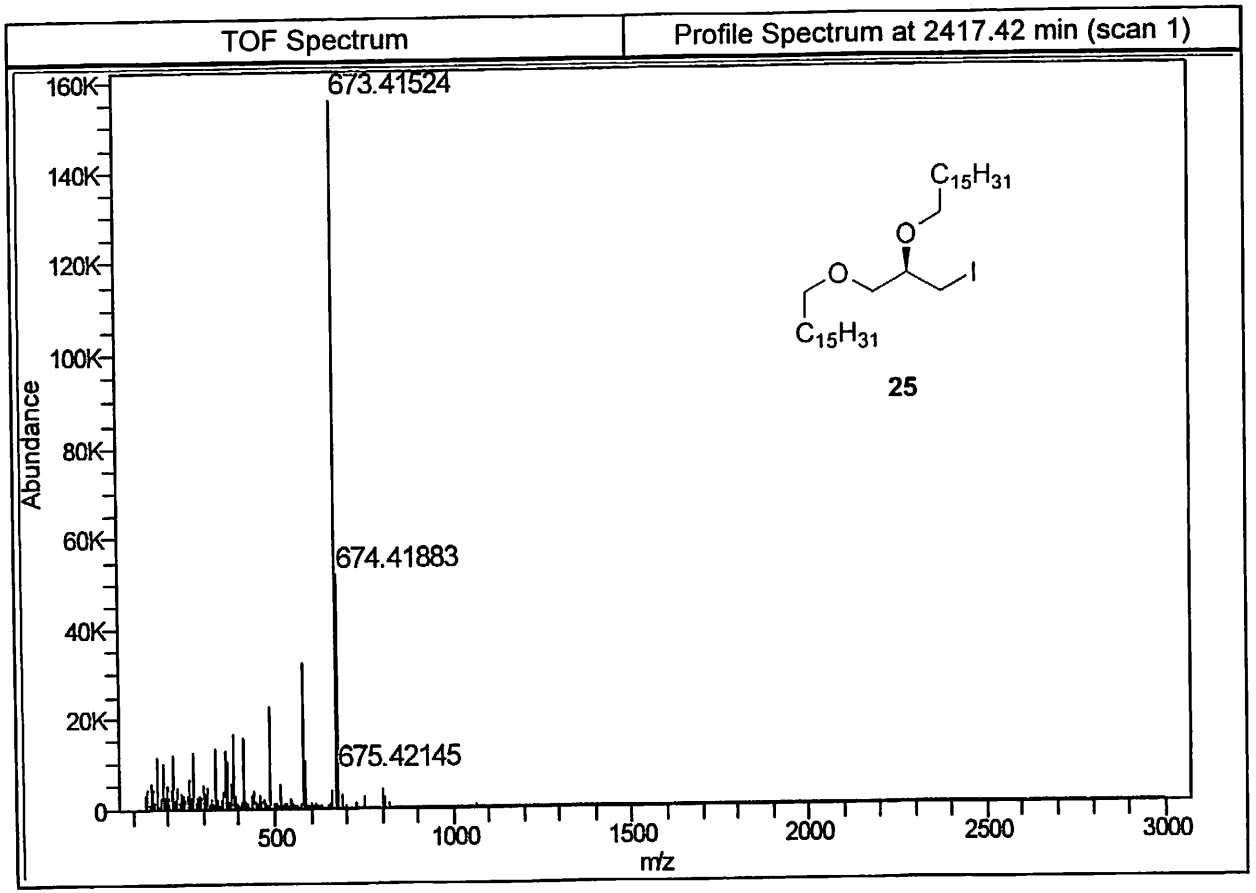

TOF Spectrum
Profile Spectrum at 7168.70 min (scan 1)
717.52427
718.52822
719.52822
Abundance
65K
60K
55K
50K
45K
40K
35K
30K
25K
20K
15K
10K
5K
0
500
1000
1500
2000
2500
3000
m/z
C15H31
O
O
OTs
C15H31
24



^{1}H NMR Spectrum

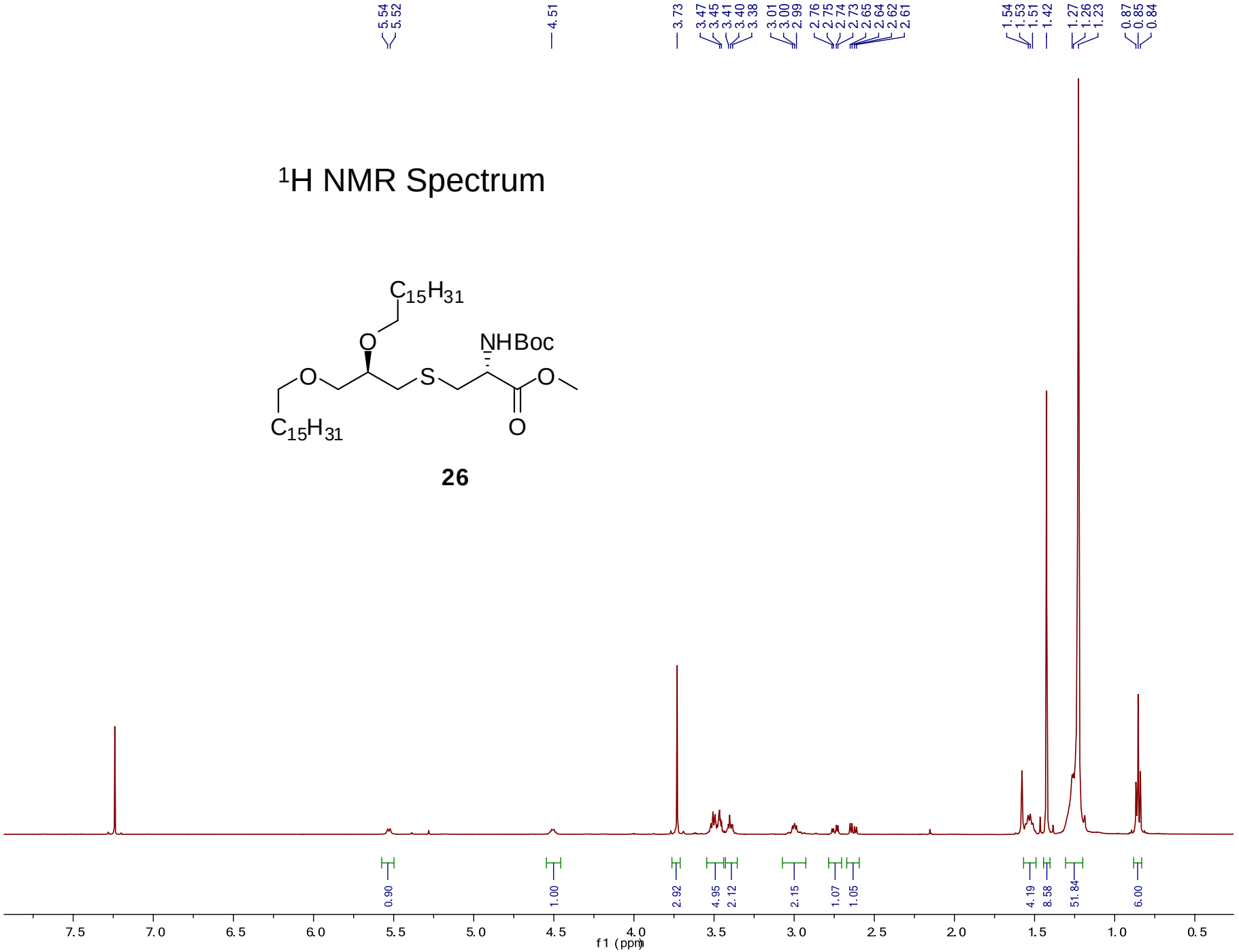
25


76.40
70.86
70.73
69.25
30.91
28.69
28.65
28.45
28.35
25.09
25.07
21.68
13.11
6.39
13C NMR Spectrum
C15H31
O
O
I
C15H31
25
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)


TOF Spectrum
Profile Spectrum at 2417.42 min (scan 1)
673.41524
674.41883
675.42145
Abundance
m/z
160K
140K
120K
100K
80K
60K
40K
20K
0
500
1000
1500
2000
2500
3000
C15H31
O
O
I
C15H31
25

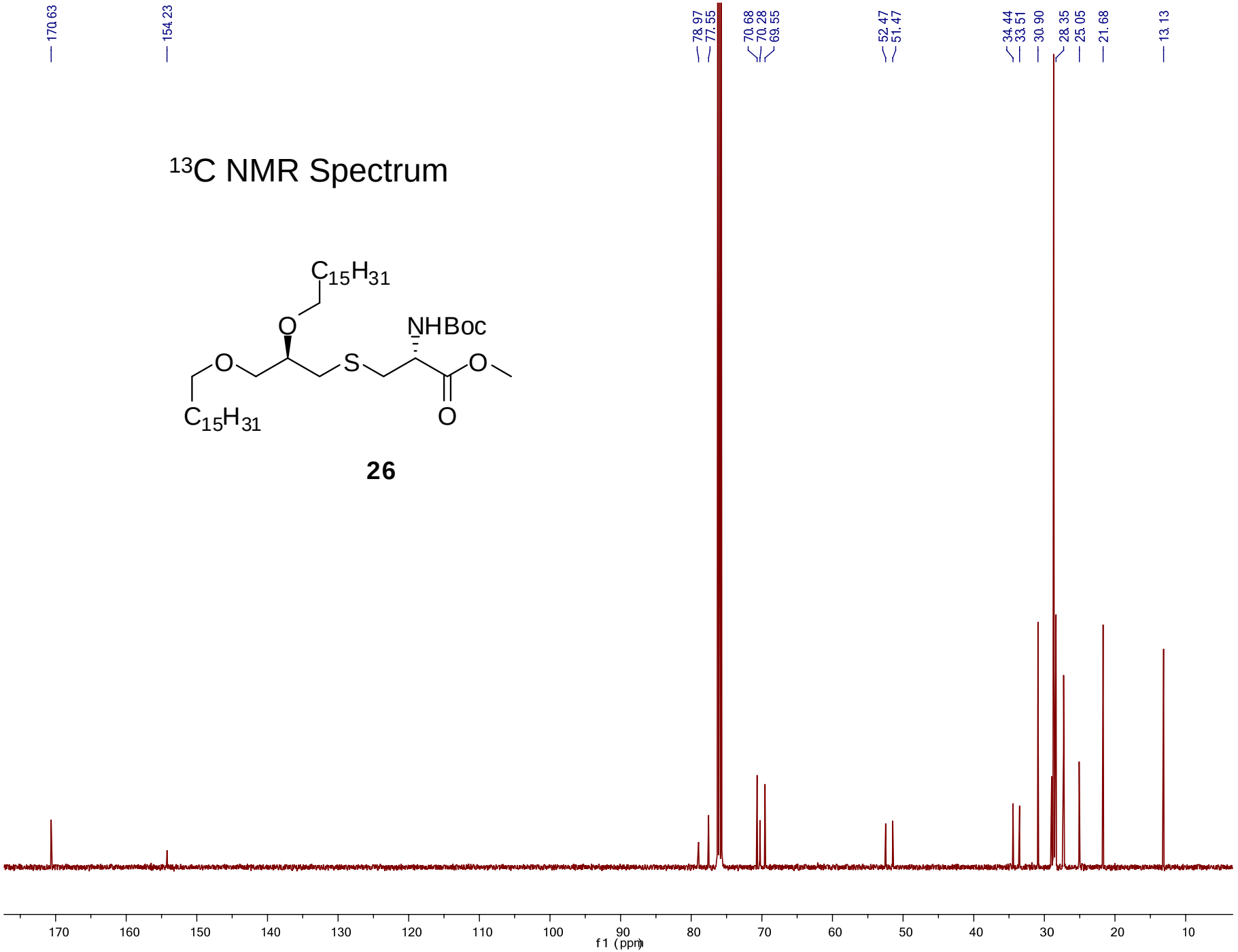
^{1}H NMR Spectrum

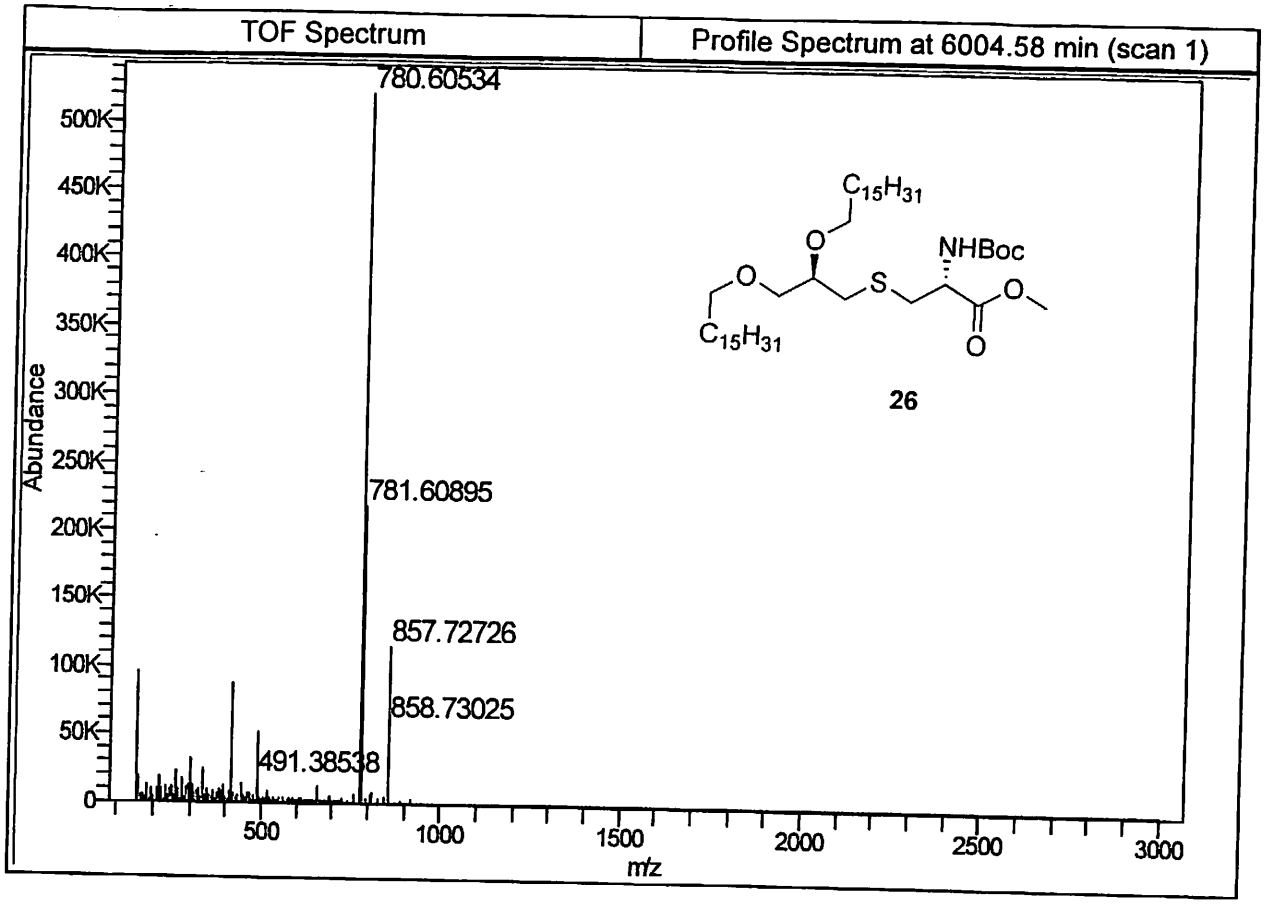
26



^{13}C NMR Spectrum

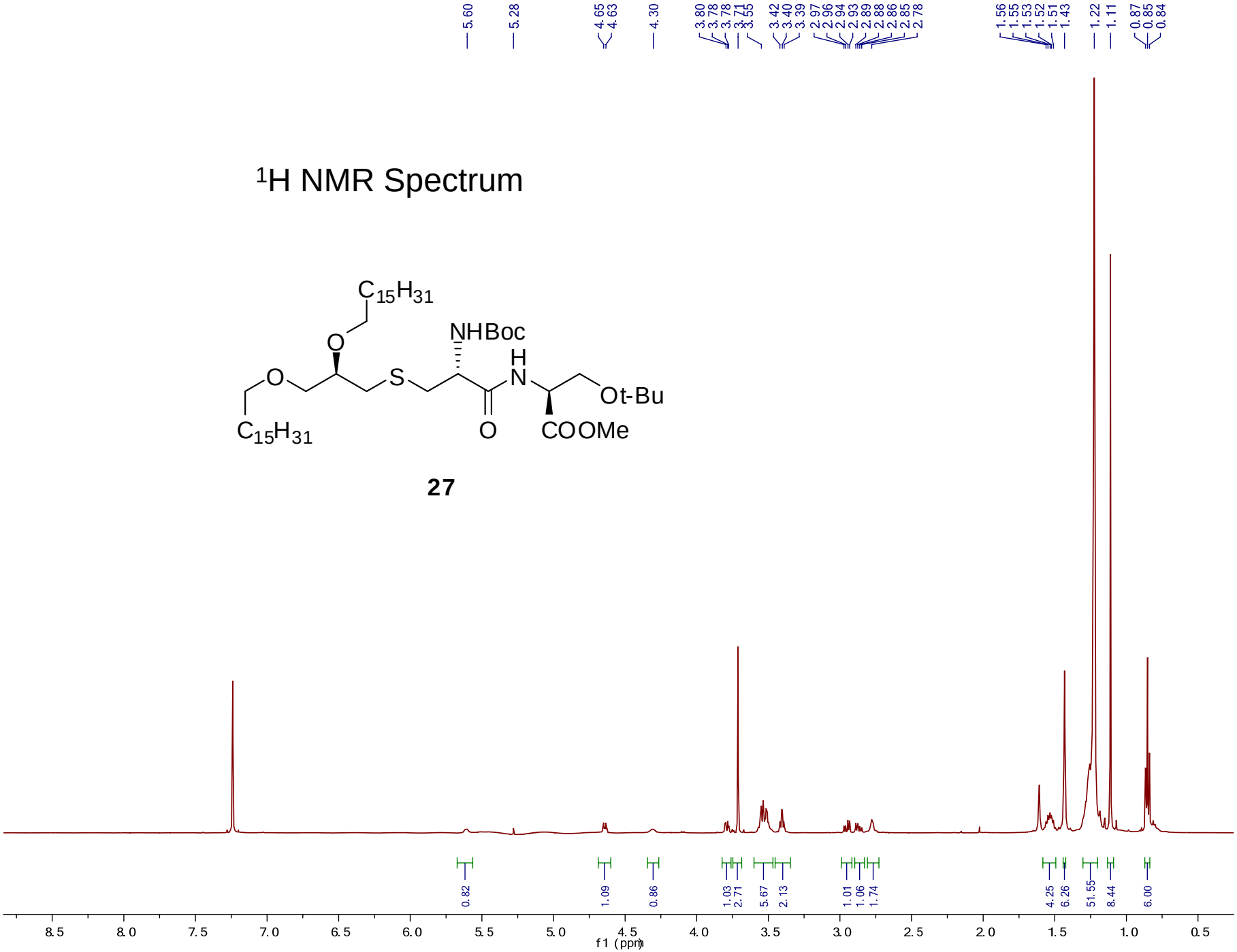
26




TOF Spectrum
Profile Spectrum at 6004.58 min (scan 1)
780.60534
781.60895
857.72726
858.73025
491.38538
Abundance
500K
450K
400K
350K
300K
250K
200K
150K
100K
50K
0
500
1000
1500
2000
2500
3000
m/z
C15H31
O
NHBoc
S
O
O
C15H31
O
26

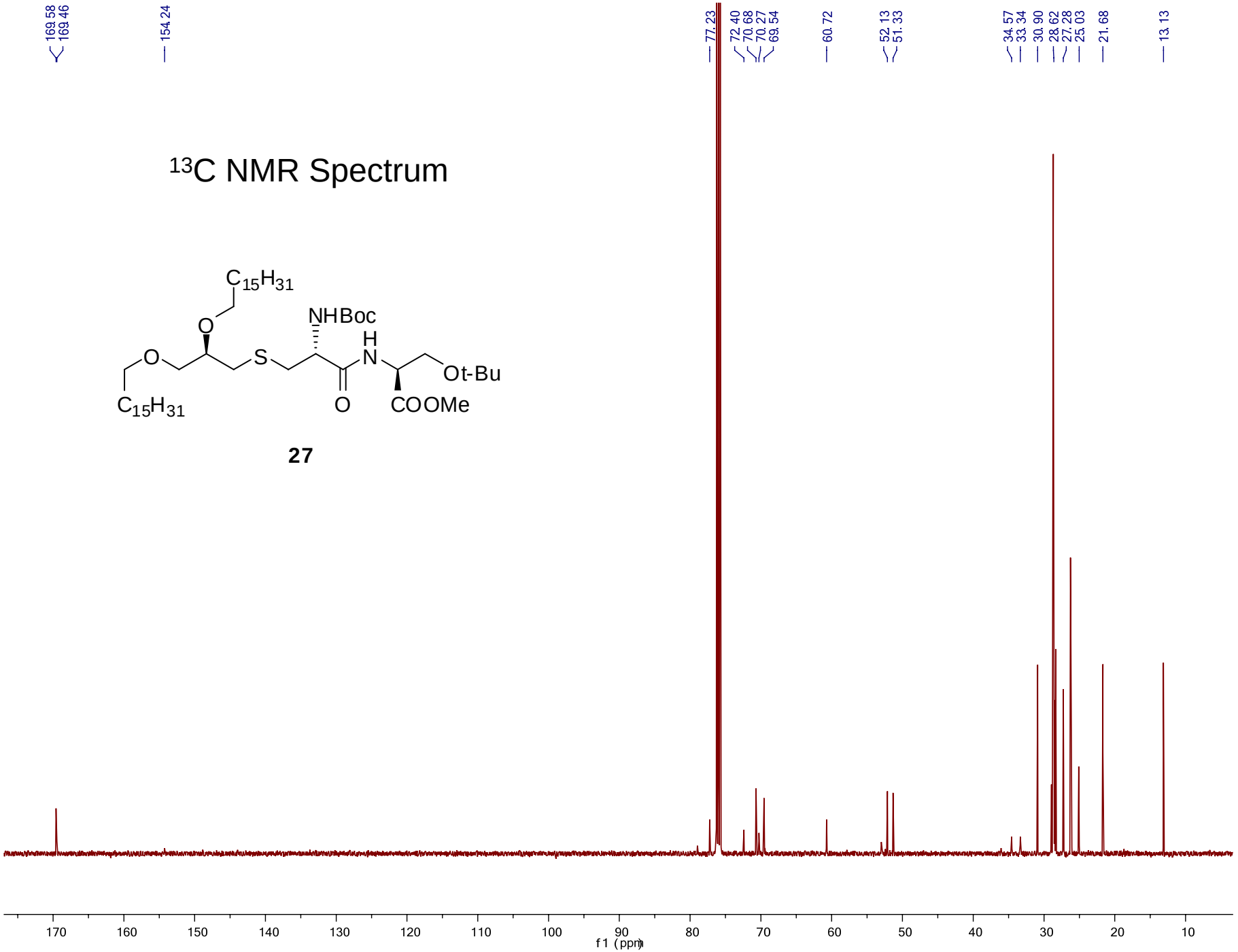
^{1}H NMR Spectrum

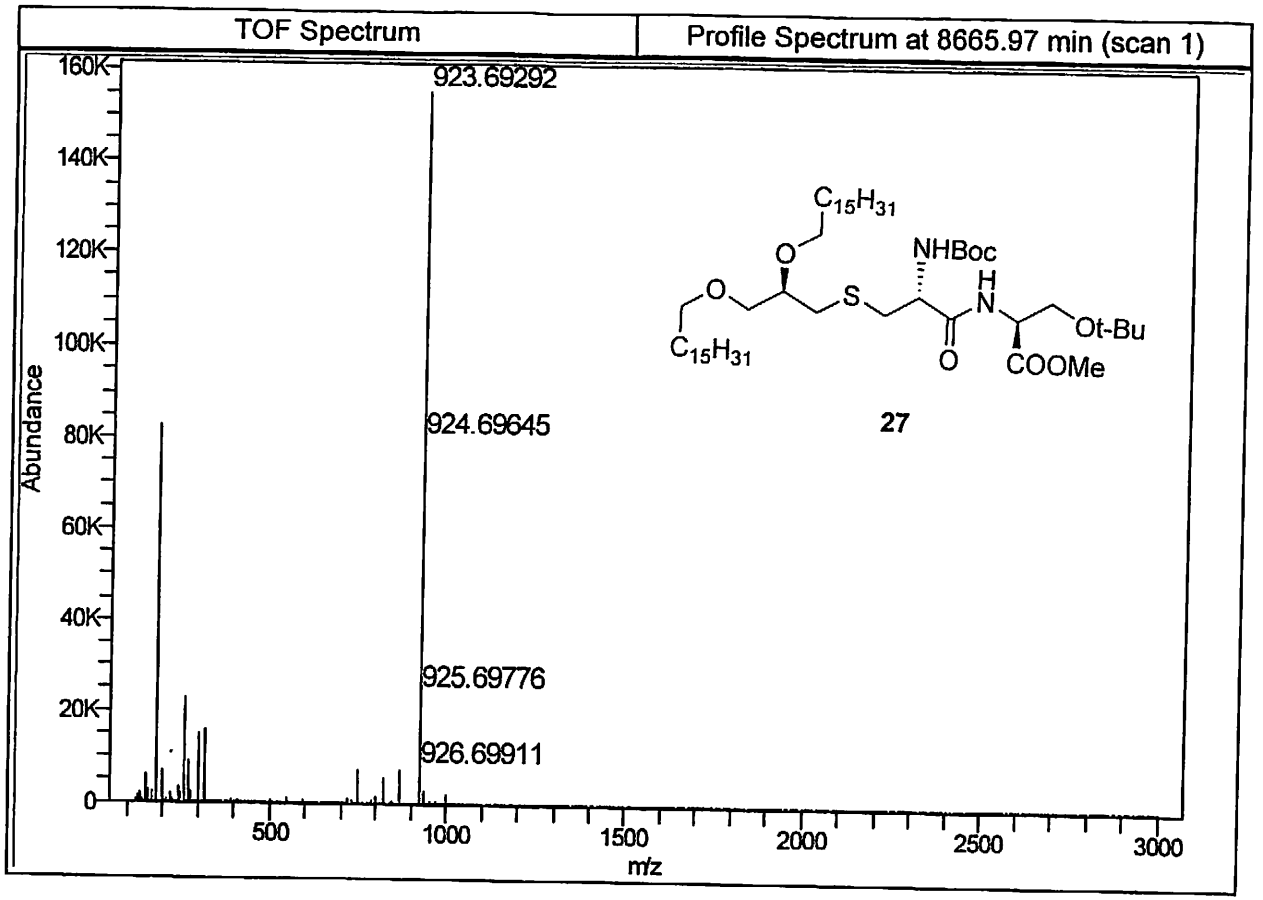
27



^{13}C NMR Spectrum

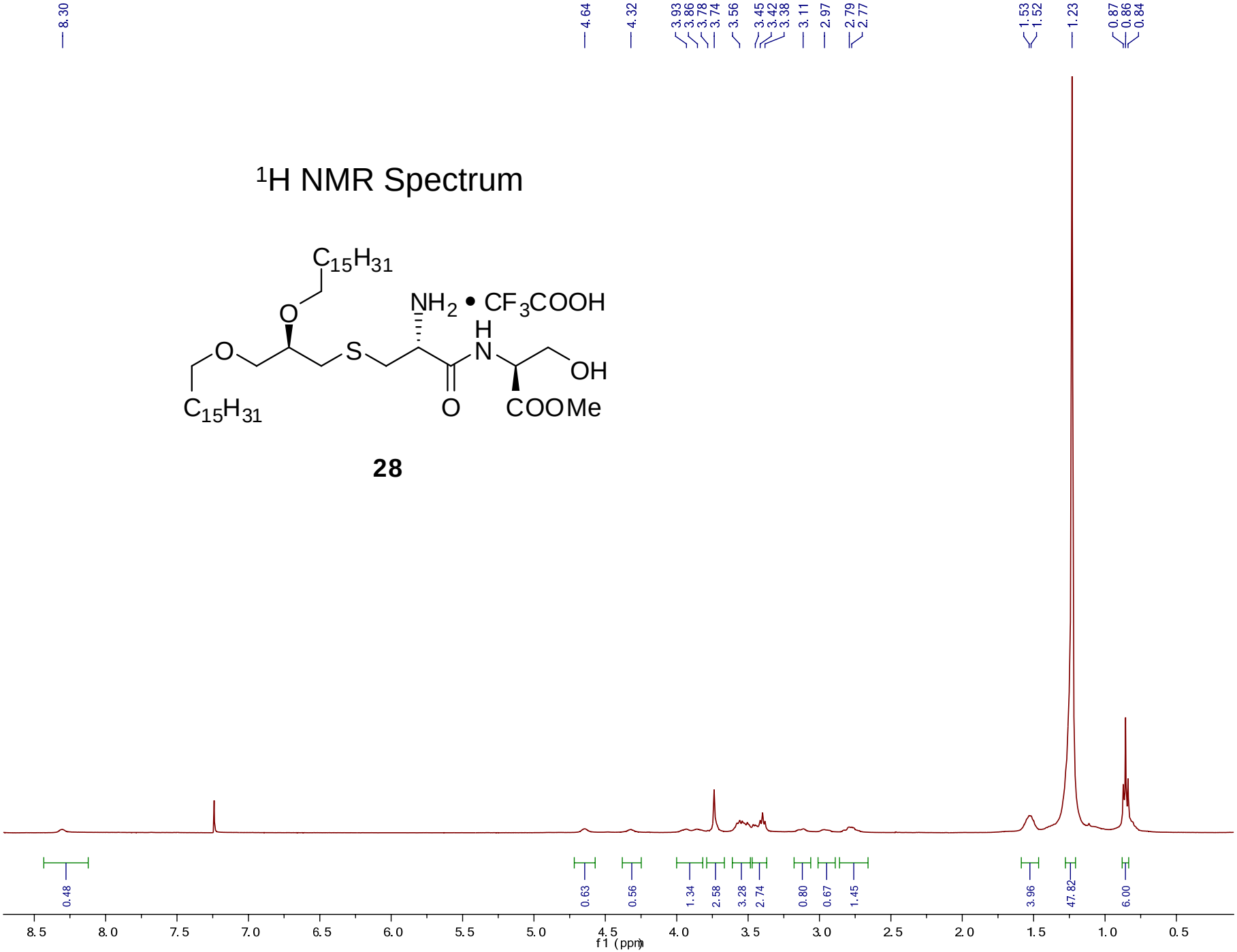
27




TOF Spectrum
Profile Spectrum at 8665.97 min (scan 1)
923.69292
924.69645
925.69776
926.69911
Abundance
m/z
160K
140K
120K
100K
80K
60K
40K
20K
0
500
1000
1500
2000
2500
3000
C15H31
O
NHBoc
H
N
S
O
C15H31
O
Ot-Bu
COOMe
27

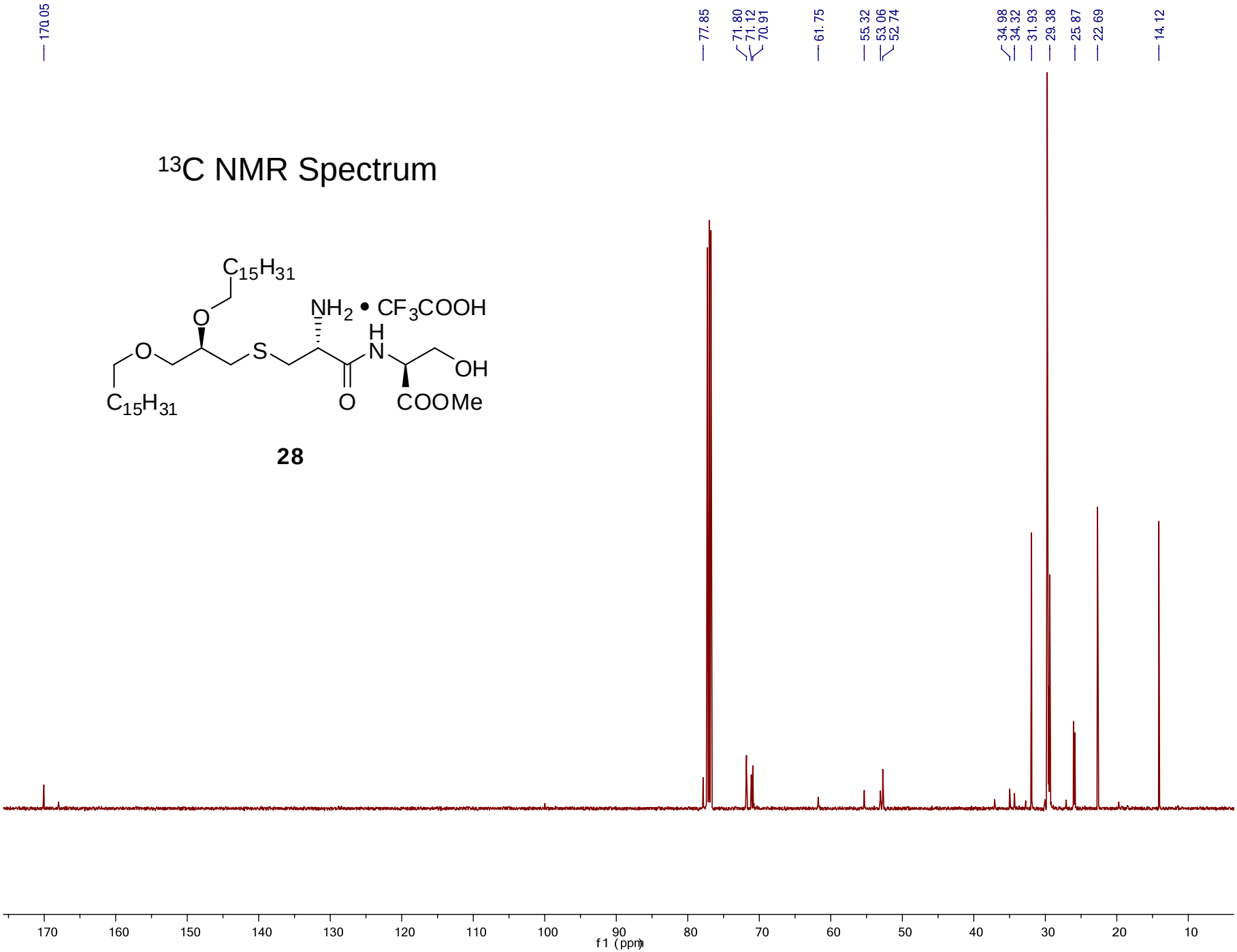
^{1}H NMR Spectrum

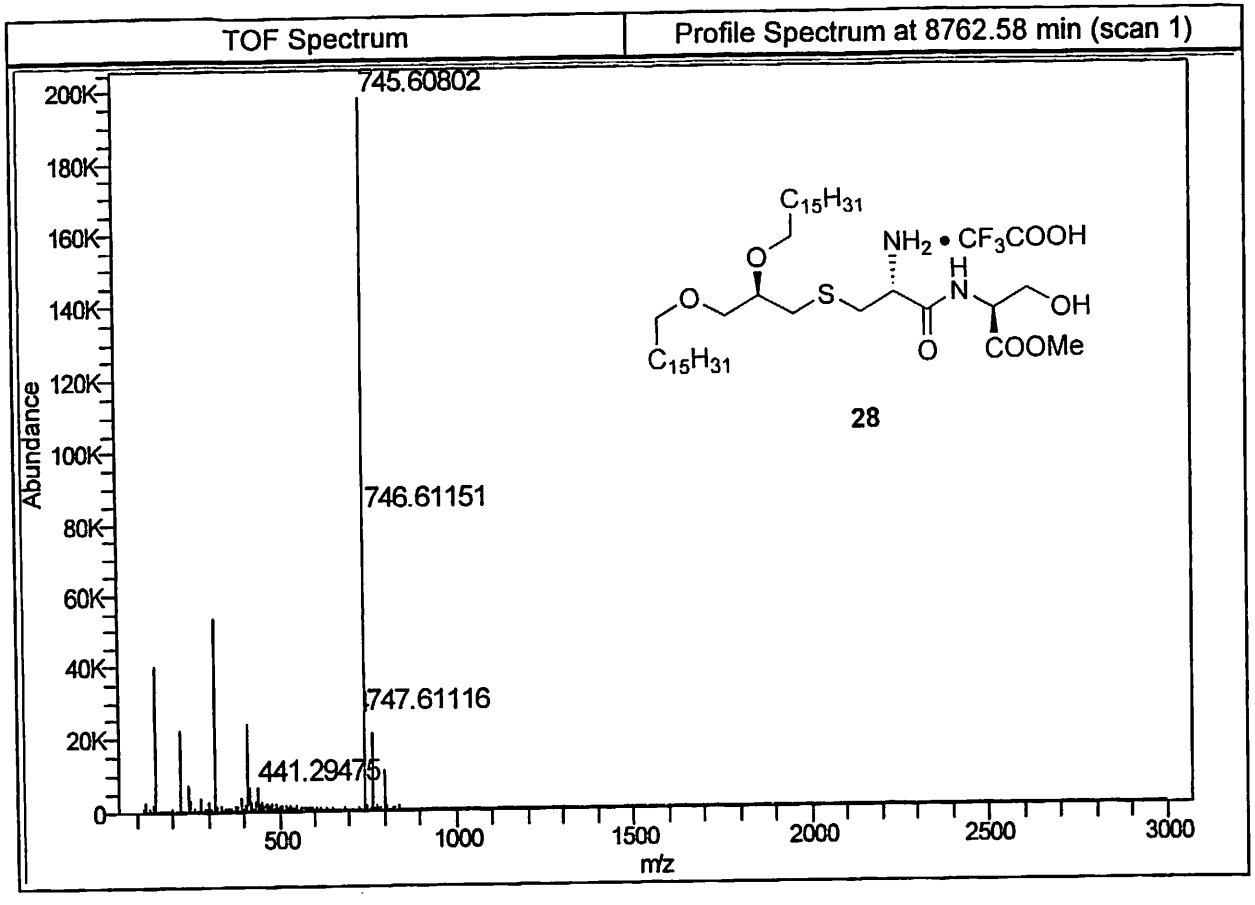
28



^{13}C NMR Spectrum

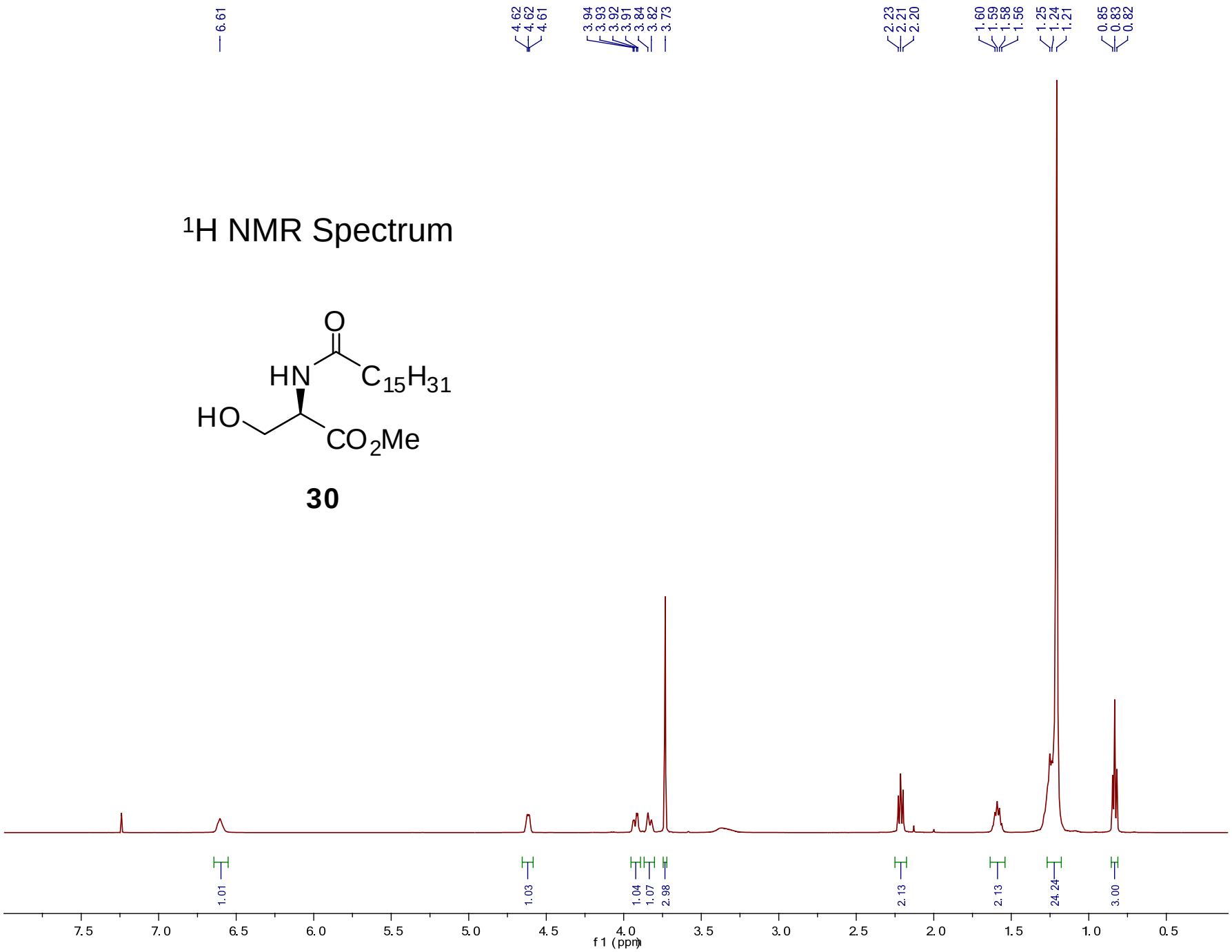
28




TOF Spectrum
Profile Spectrum at 8762.58 min (scan 1)
745.60802
746.61151
747.61116
441.29475
Abundance
m/z
200K
180K
160K
140K
120K
100K
80K
60K
40K
20K
0
500
1000
1500
2000
2500
3000
C15H31
O
NH2 • CF3COOH
H
N
S
O
OH
O
C15H31
O
COOMe
28

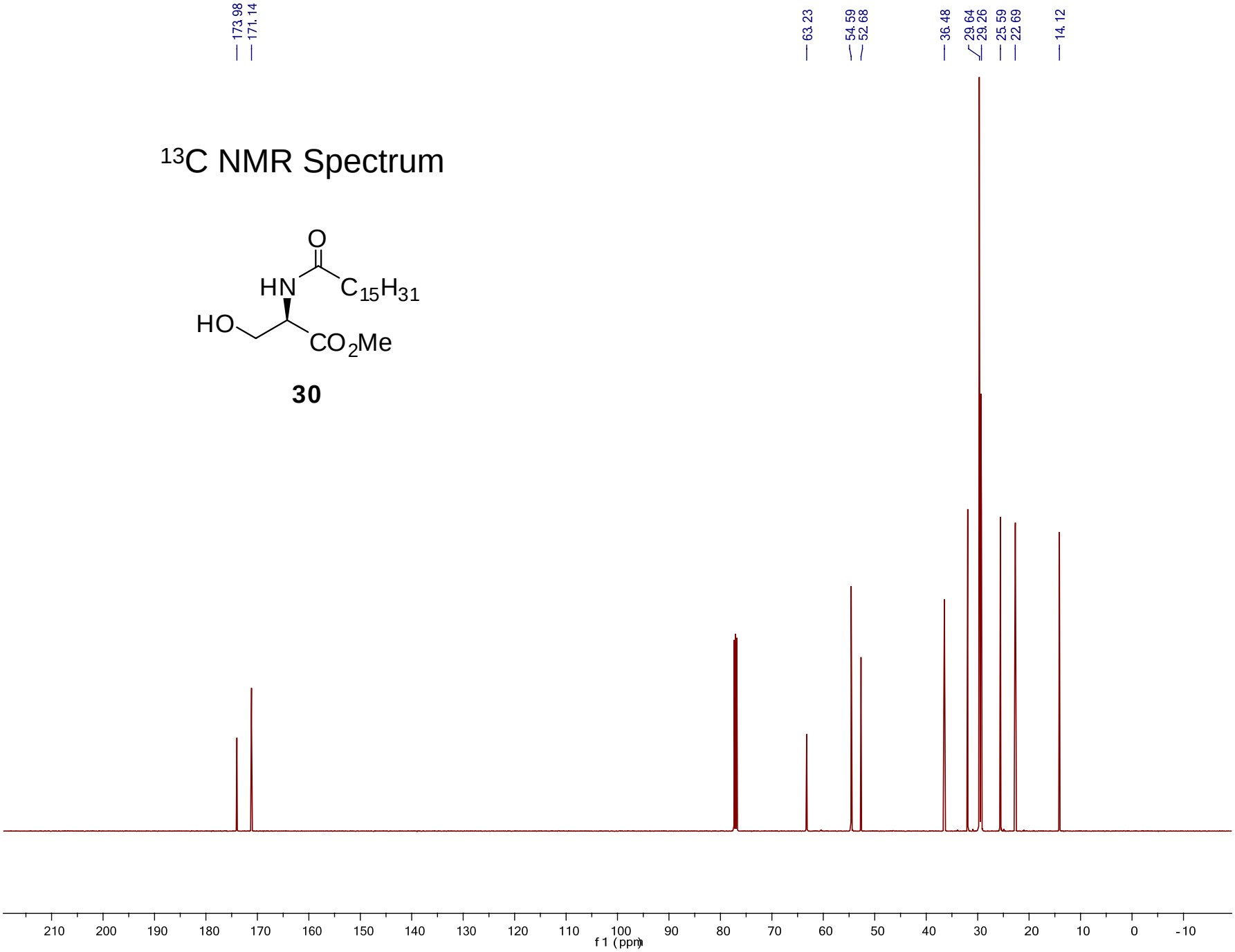
^{1}H NMR Spectrum

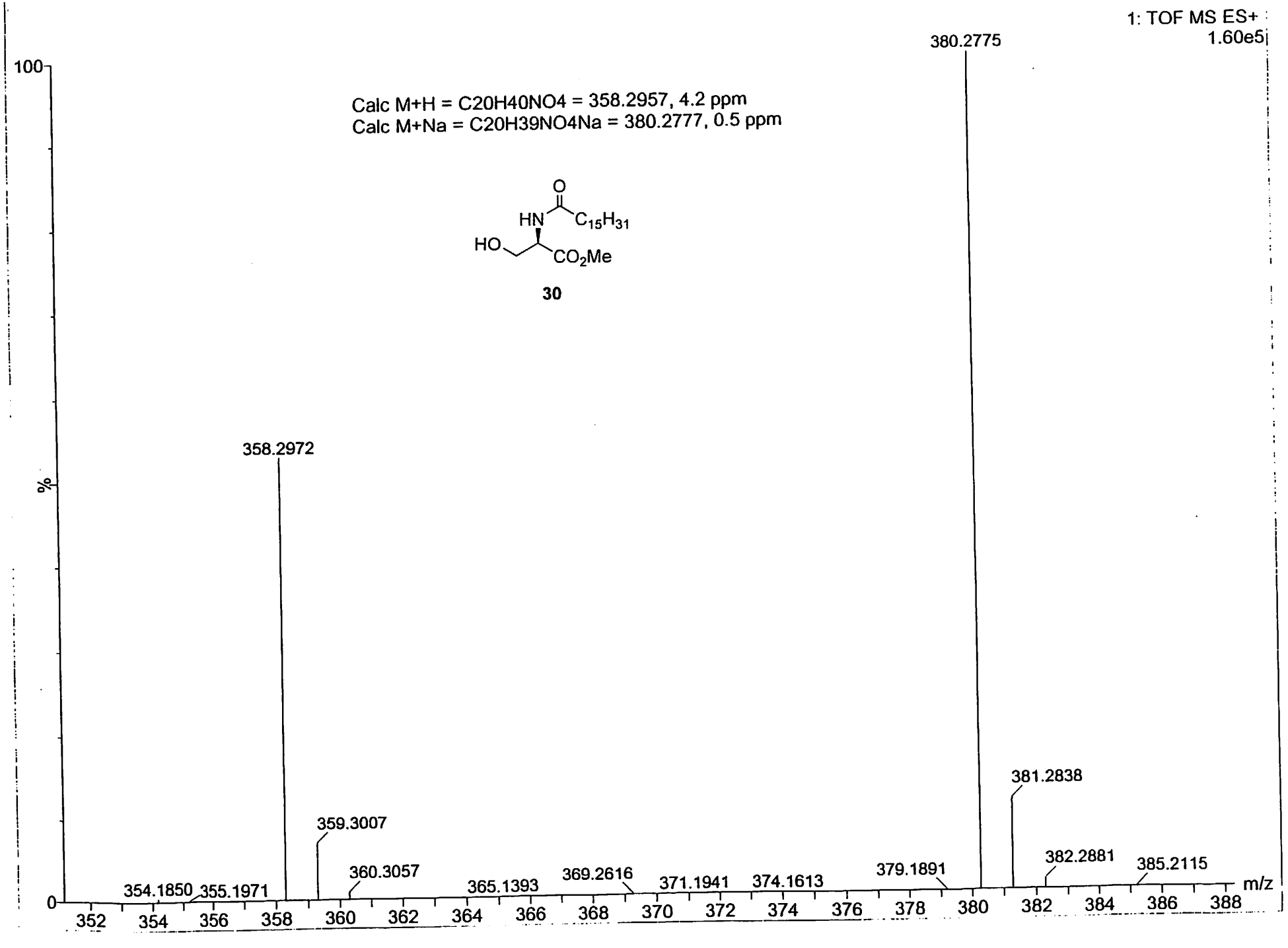
30



^{13}C NMR Spectrum

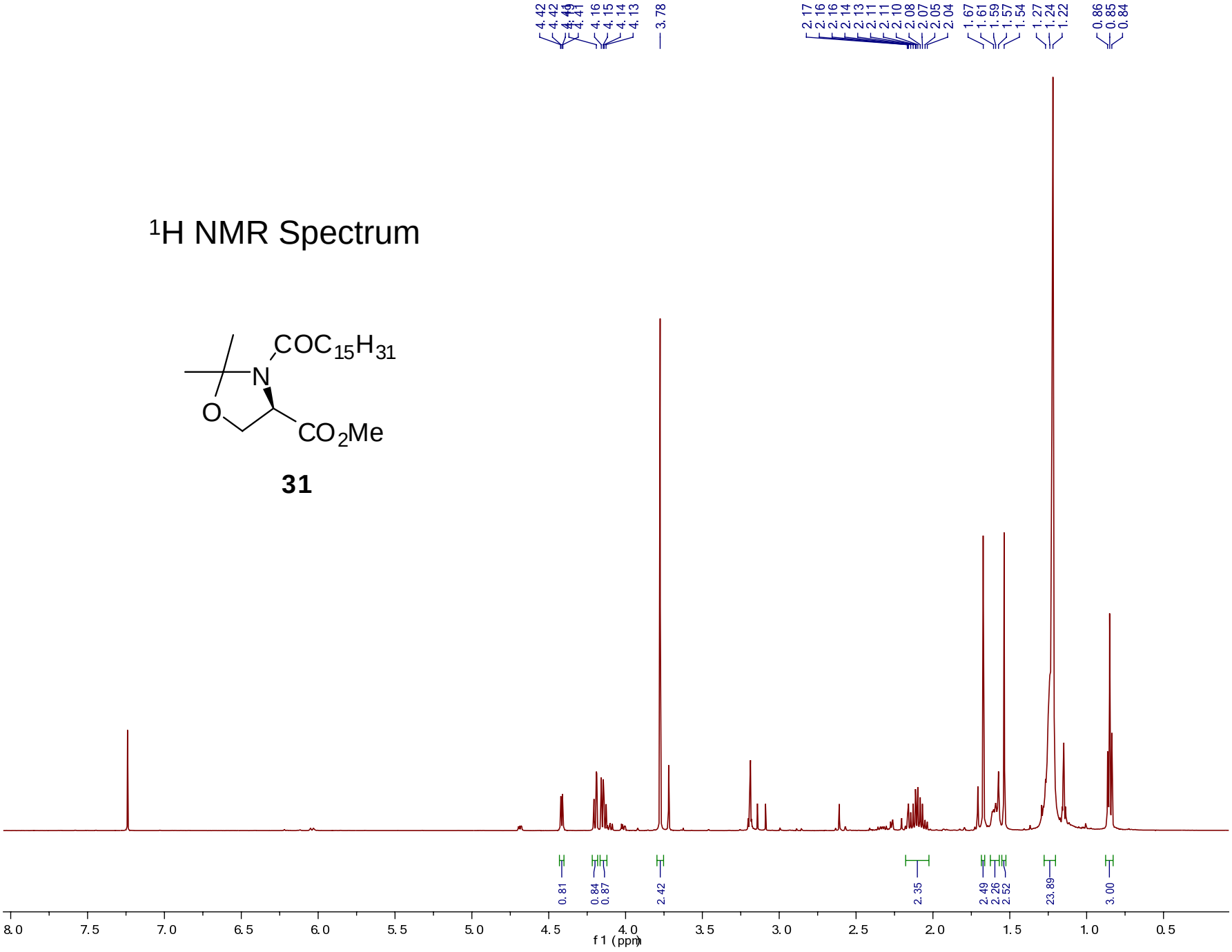
30

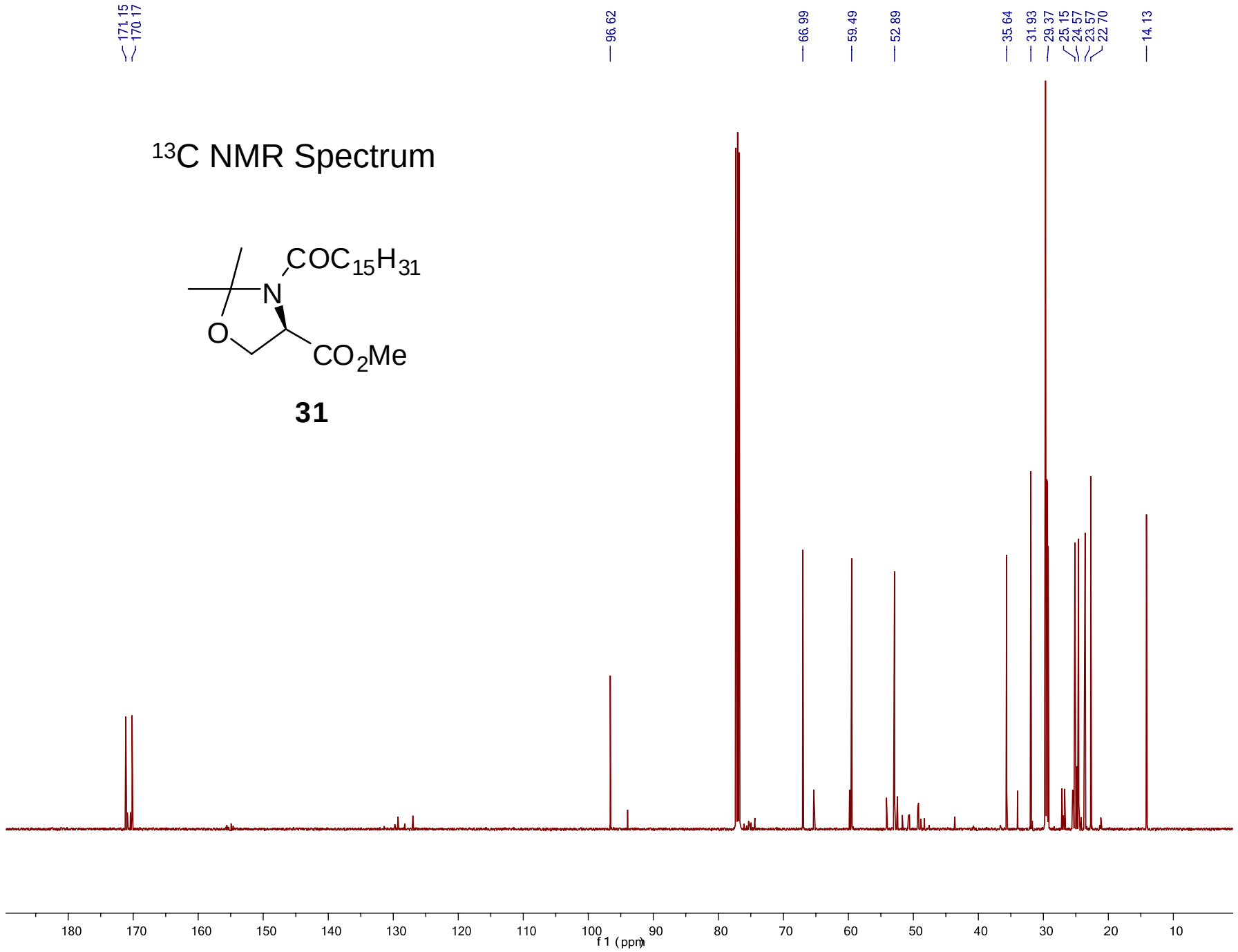


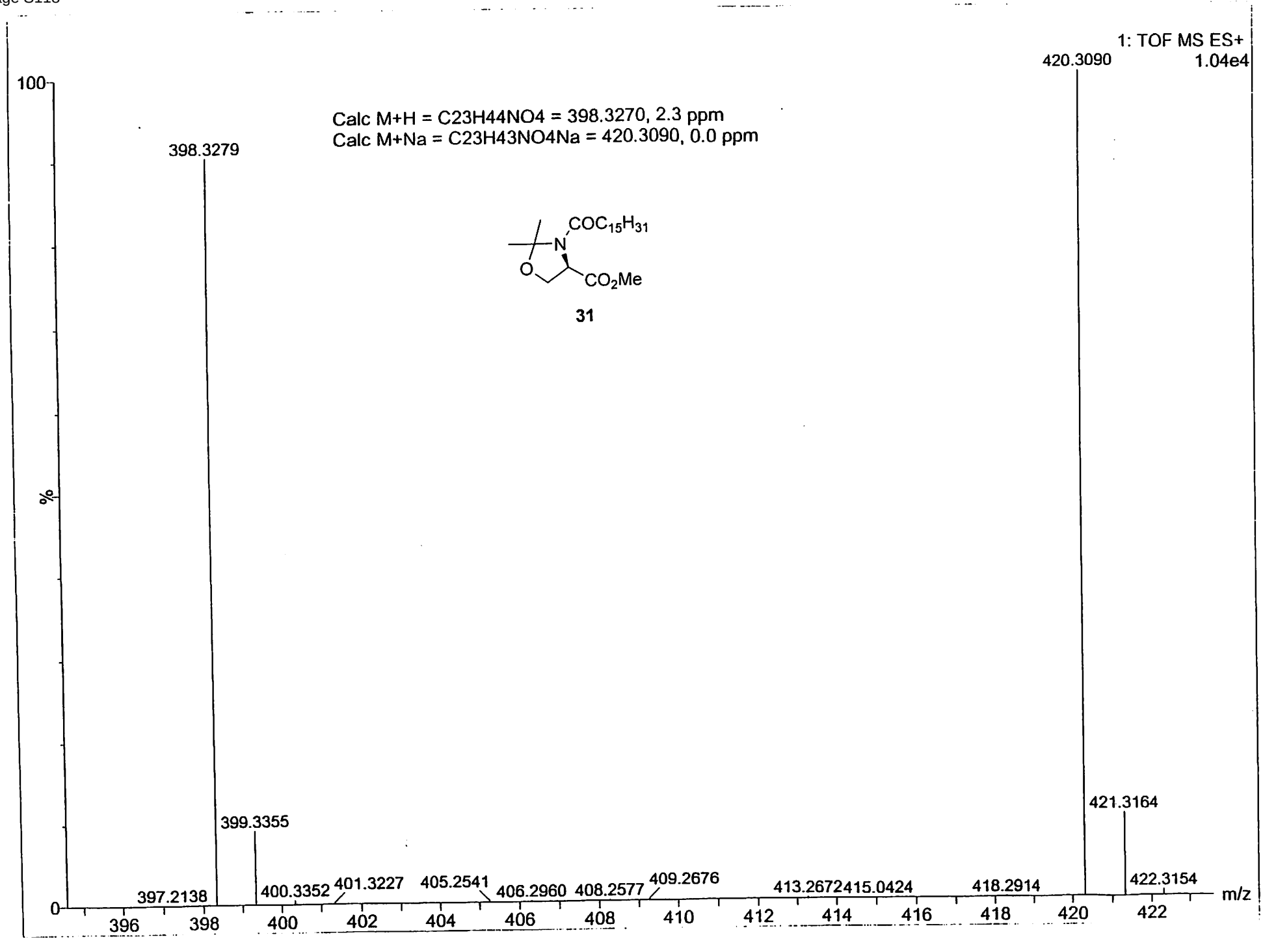

1: TOF MS ES+
1.60e5
100
%
0
Calc M+H = C20H40NO4 = 358.2957, 4.2 ppm
Calc M+Na = C20H39NO4Na = 380.2777, 0.5 ppm
O
HN
C15H31
HO
CO2Me
30
380.2775
358.2972
381.2838
359.3007
382.2881
385.2115
360.3057
379.1891
354.1850
355.1971
365.1393
369.2616
371.1941
374.1613
m/z
352
354
356
358
360
362
364
366
368
370
372
374
376
378
380
382
384
386
388

^{1}H NMR Spectrum

31

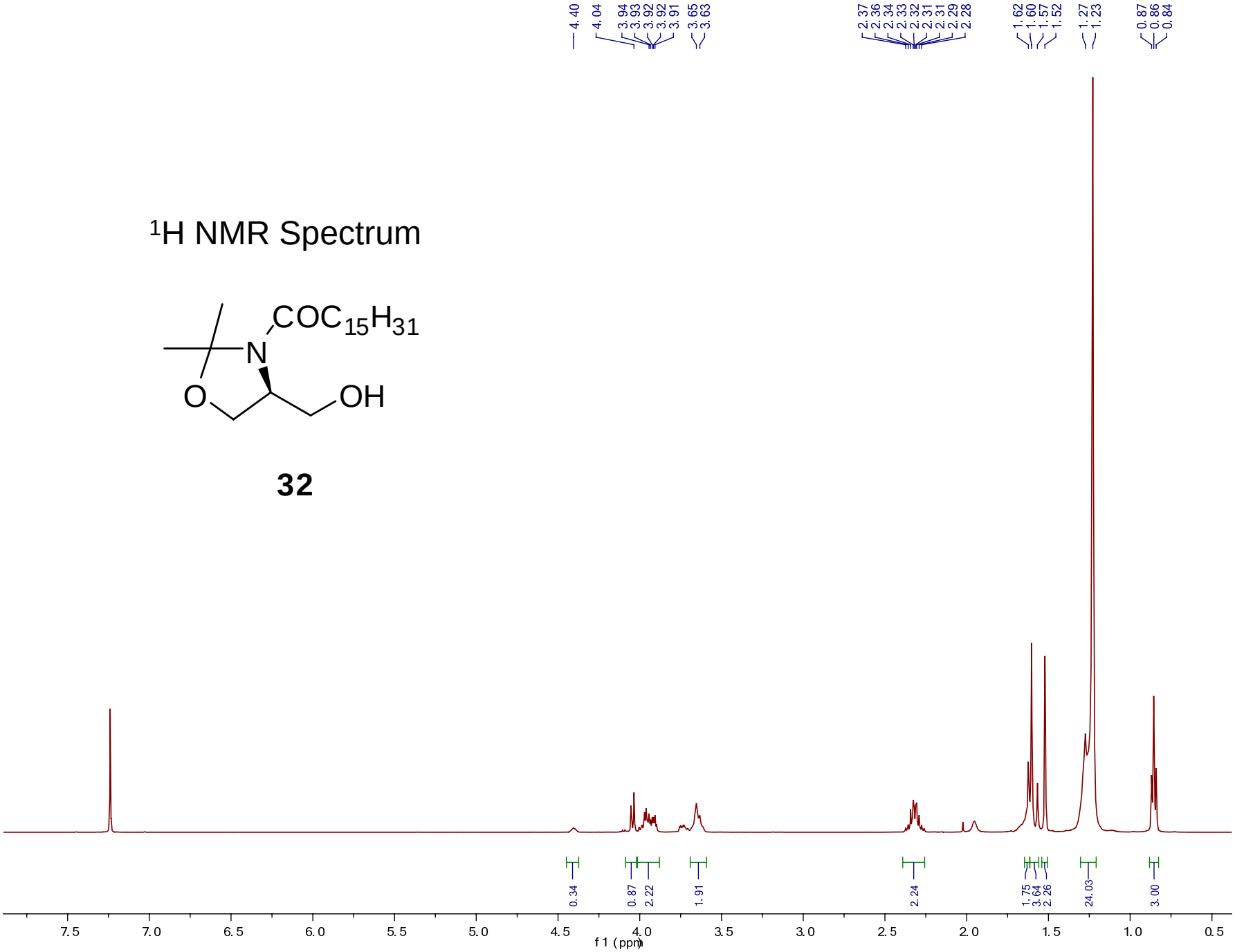


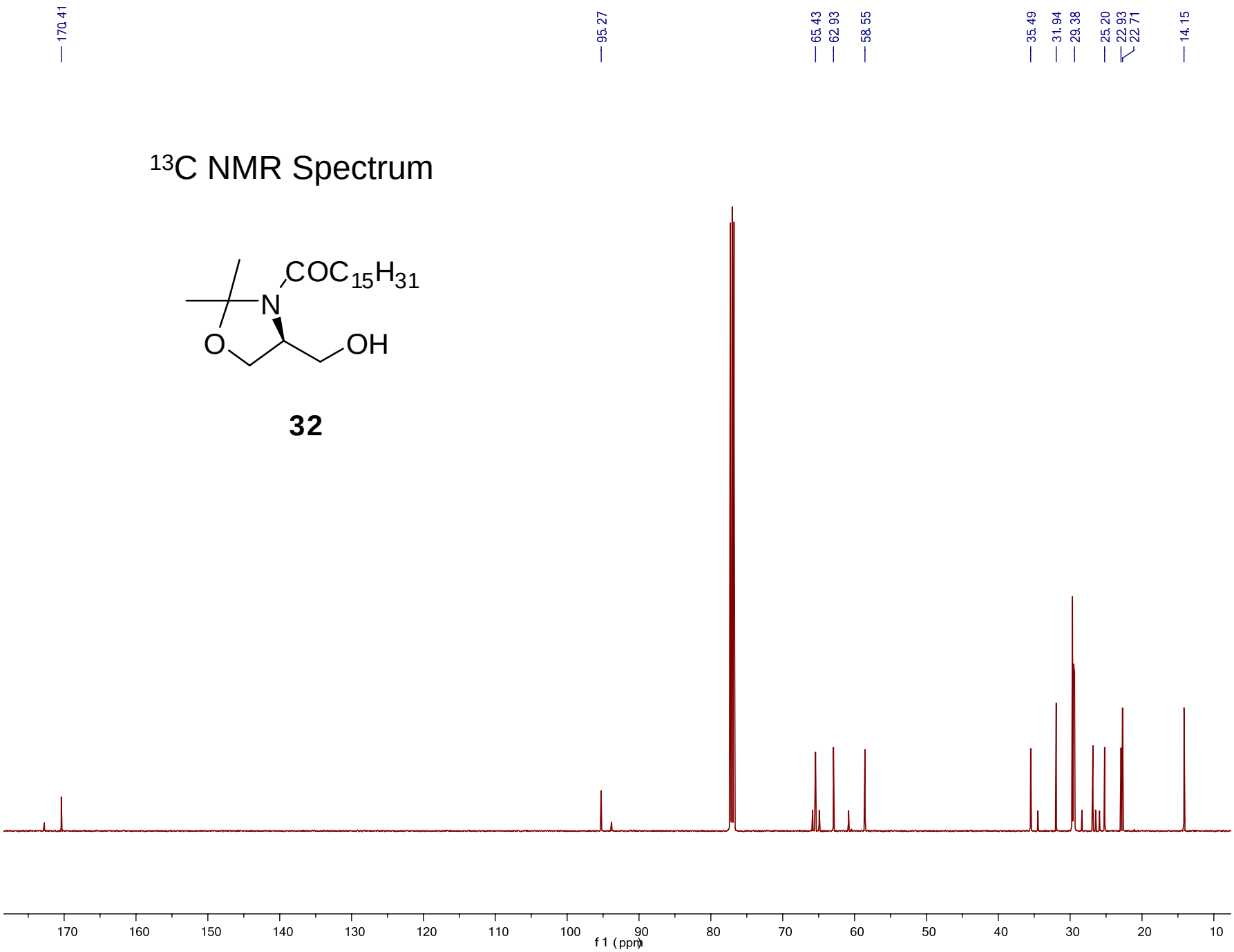

171.15
170.17
96.62
66.99
59.49
52.89
35.64
31.93
29.37
25.15
24.57
23.57
22.70
14.13
13C NMR Spectrum
COC15H31
N
O
CO2Me
31
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

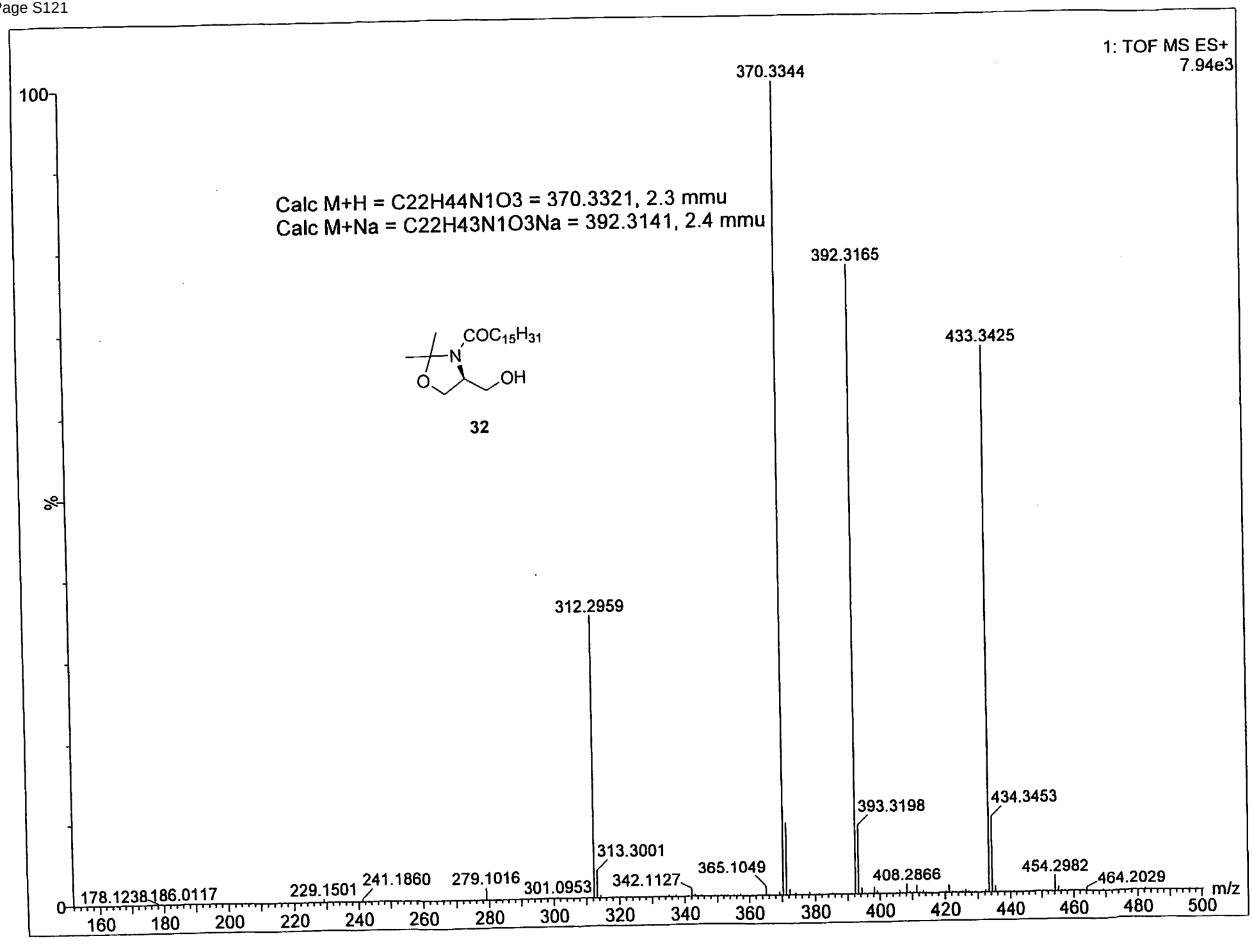

1: TOF MS ES+
1.04e4
420.3090
100
%
0
Calc M+H = C23H44NO4 = 398.3270, 2.3 ppm
Calc M+Na = C23H43NO4Na = 420.3090, 0.0 ppm
398.3279
COC15H31
N
O
CO2Me
31
399.3355
421.3164
397.2138
400.3352
401.3227
405.2541
406.2960
408.2577
409.2676
413.2672
415.0424
418.2914
422.3154
m/z
396
398
400
402
404
406
408
410
412
414
416
418
420
422

^{1}H NMR Spectrum

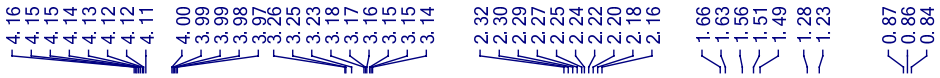
32




170.41
95.27
65.43
62.93
58.55
35.49
31.94
29.38
25.20
22.93
22.71
14.15
13C NMR Spectrum
COC15H31
N
O
OH
32
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

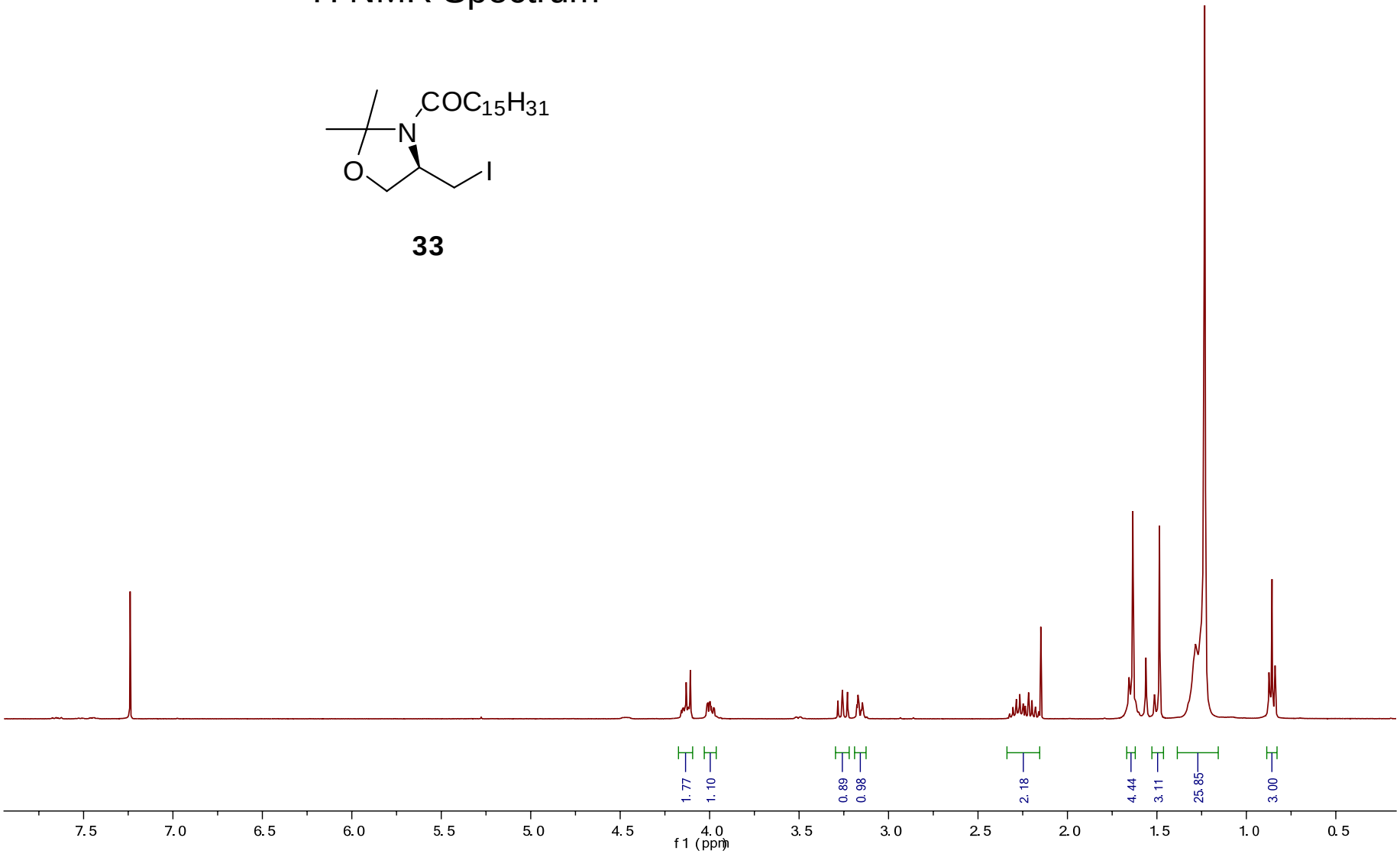

1: TOF MS ES+
7.94e3
370.3344
392.3165
433.3425
312.2959
393.3198
434.3453
313.3001
365.1049
408.2866
454.2982
464.2029
342.1127
301.0953
279.1016
241.1860
229.1501
178.1238
186.0117
100
%
0
m/z
160
180
200
220
240
260
280
300
320
340
360
380
400
420
440
460
480
500
Calc M+H = C22H44N1O3 = 370.3321, 2.3 mmu
Calc M+Na = C22H43N1O3Na = 392.3141, 2.4 mmu
COC15H31
N
O
OH

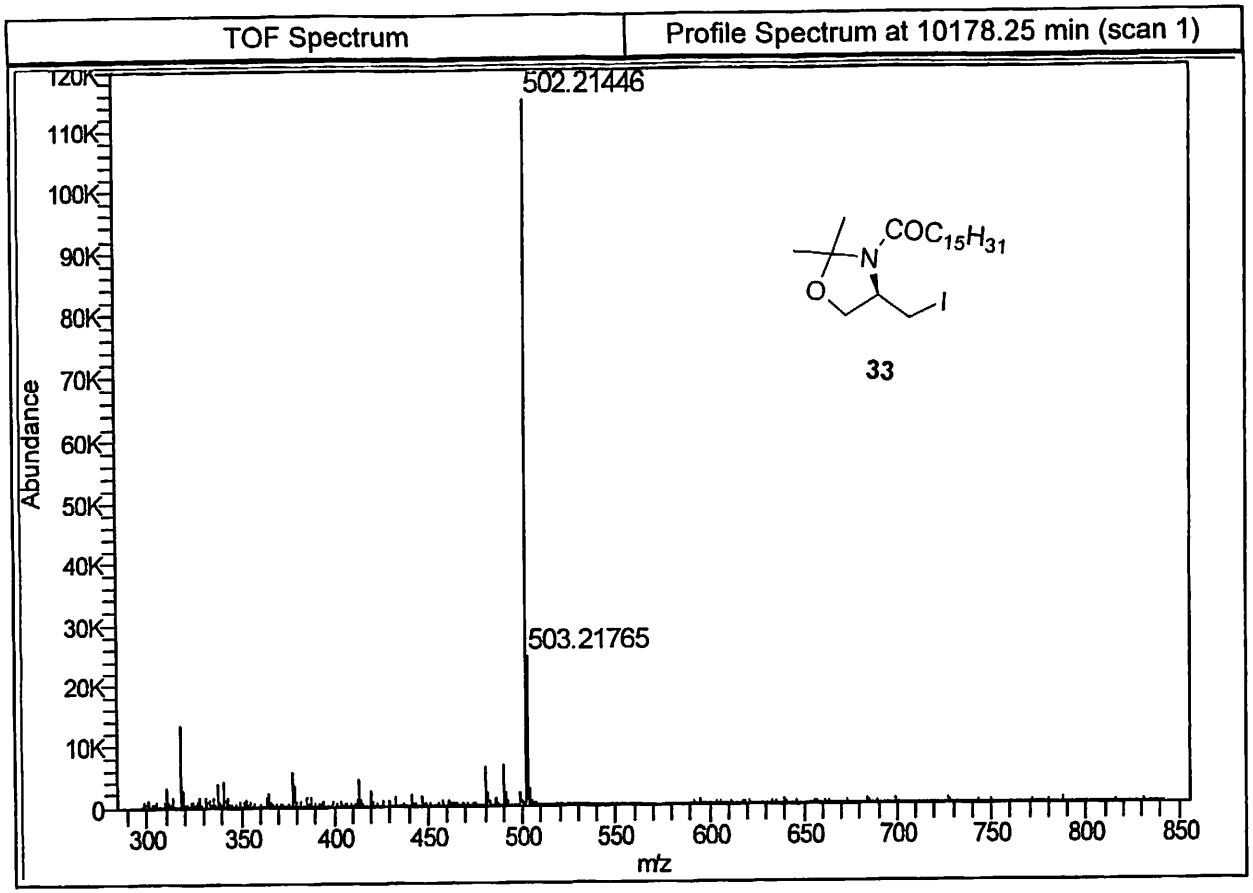
32



^{1}H NMR Spectrum

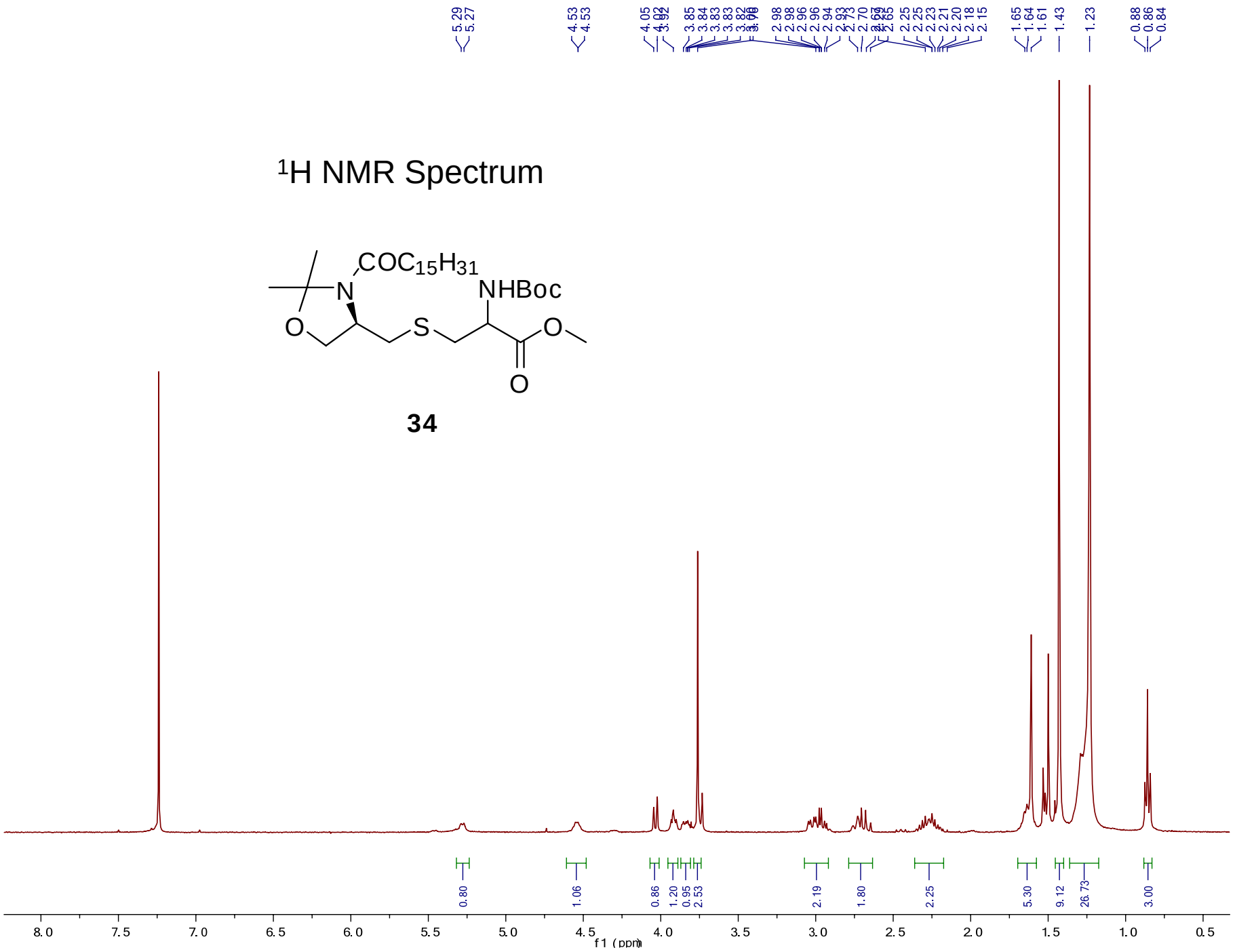
33

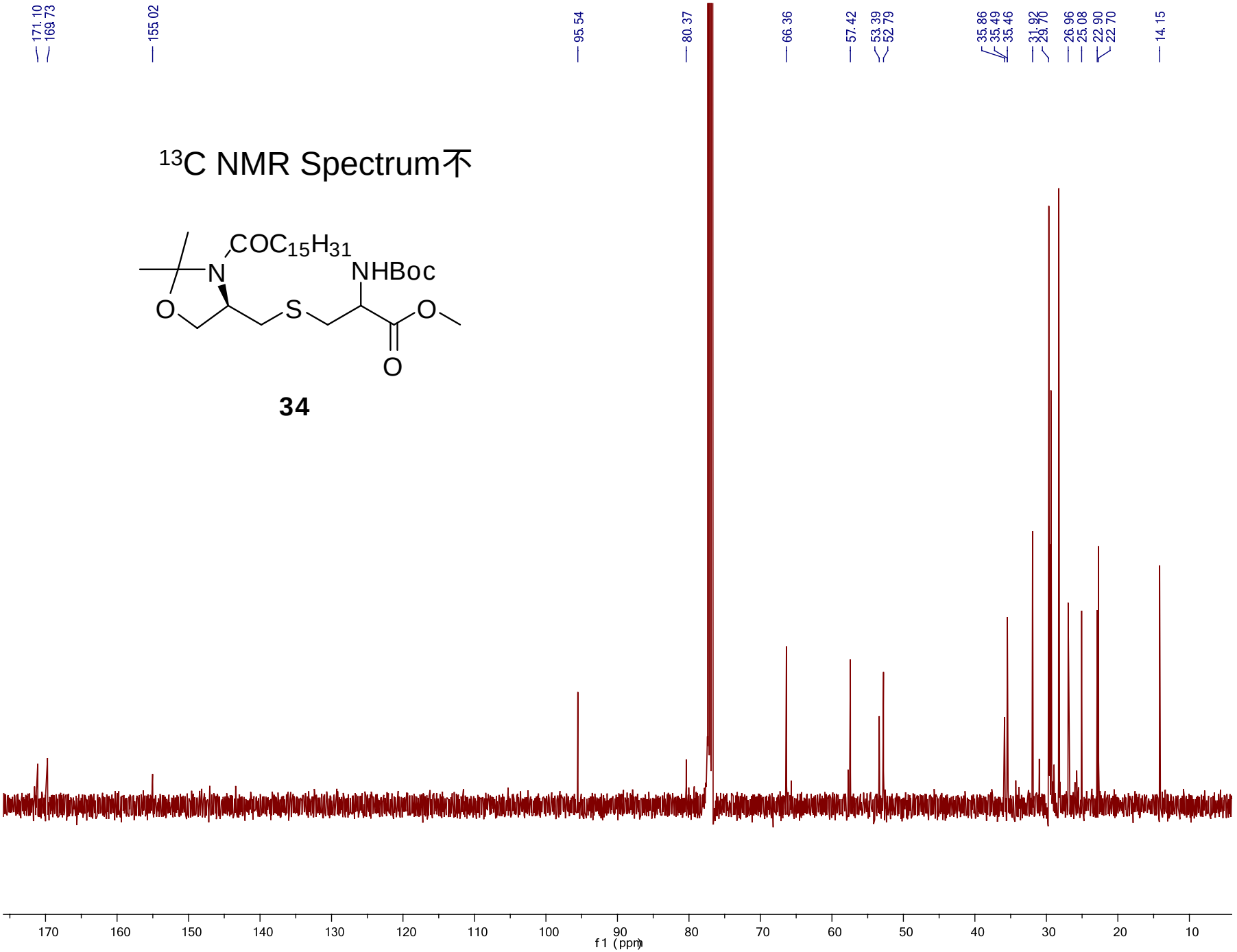


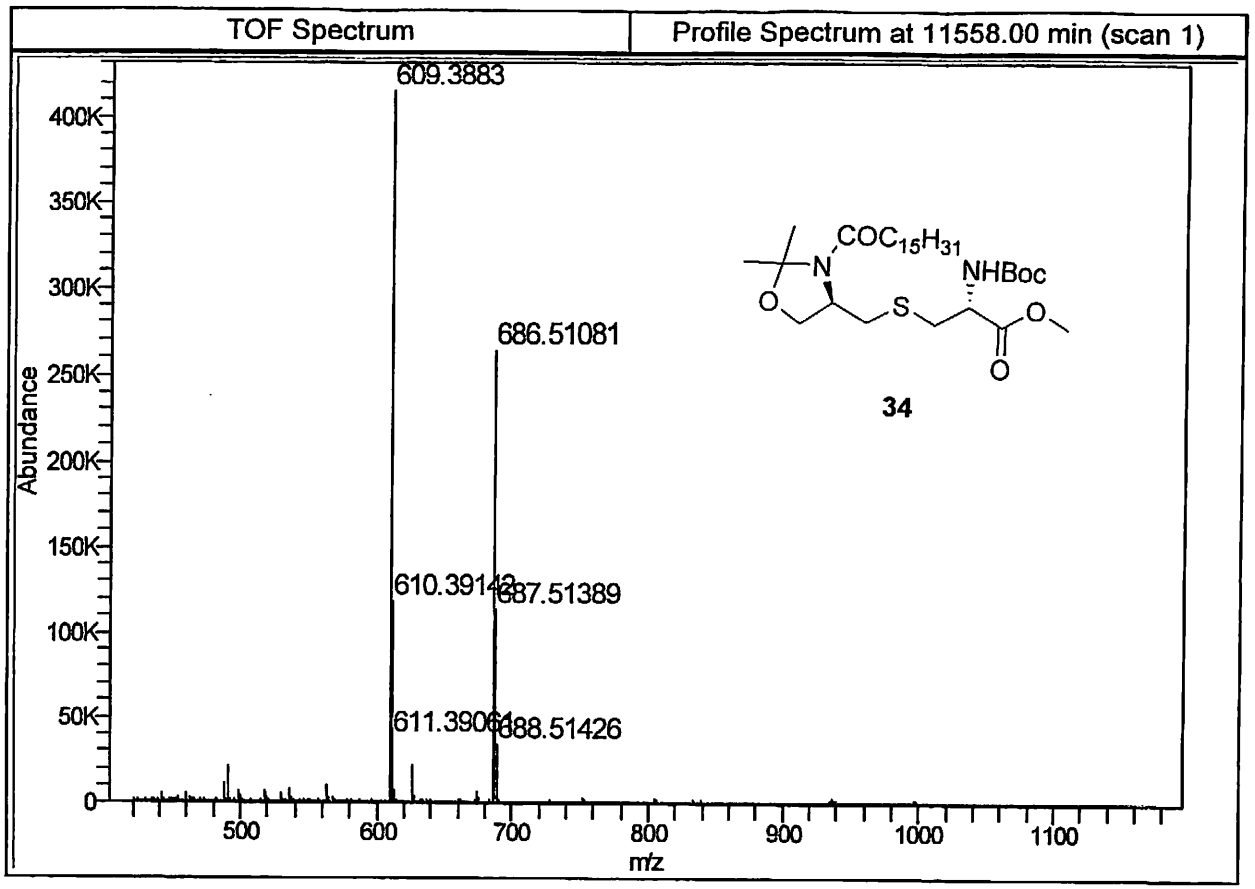

TOF Spectrum
Profile Spectrum at 10178.25 min (scan 1)
502.21446
503.21765
Abundance
m/z
120K
110K
100K
90K
80K
70K
60K
50K
40K
30K
20K
10K
0
300
350
400
450
500
550
600
650
700
750
800
850
COC15H31
N
O
I
33

^{1}H NMR Spectrum

34

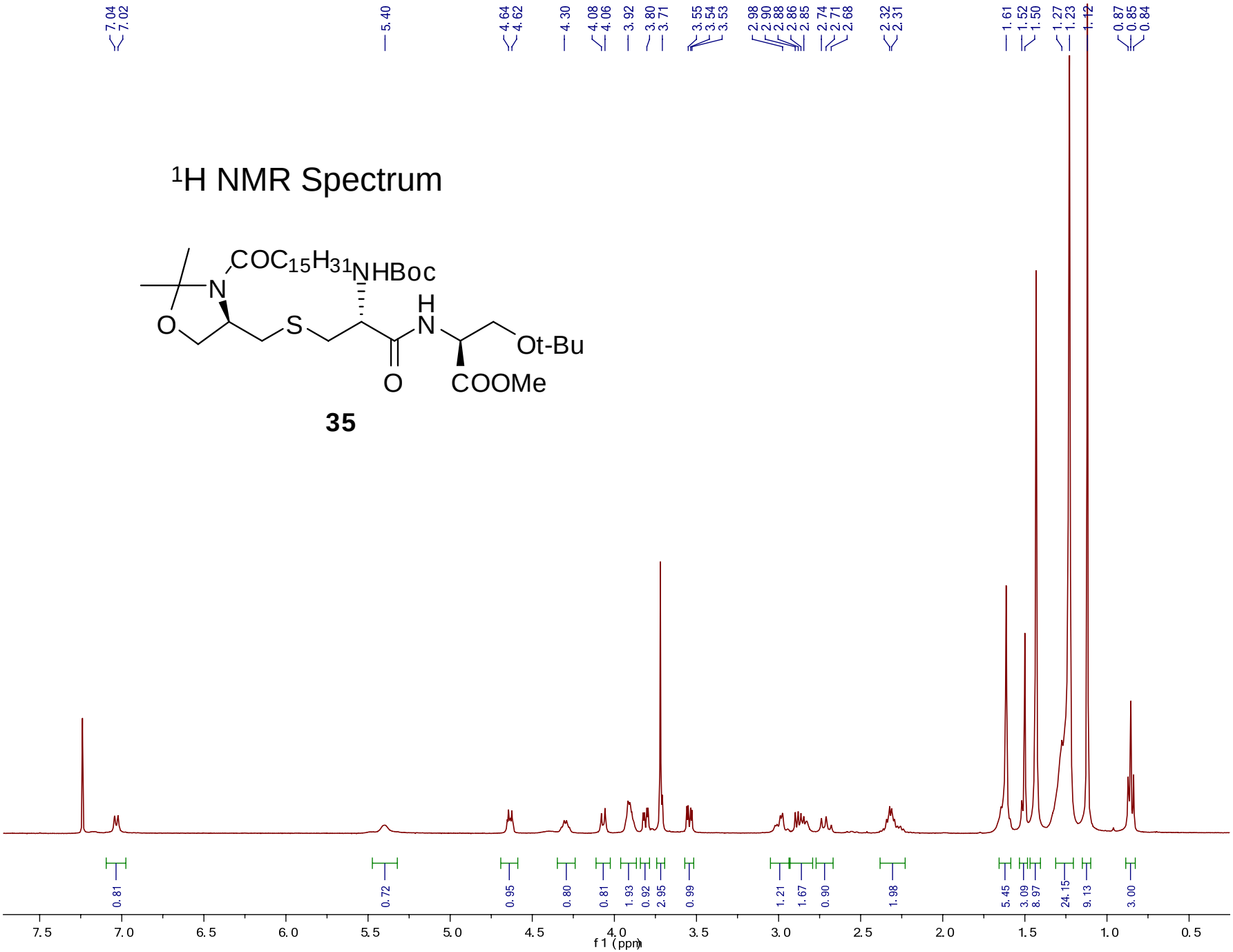


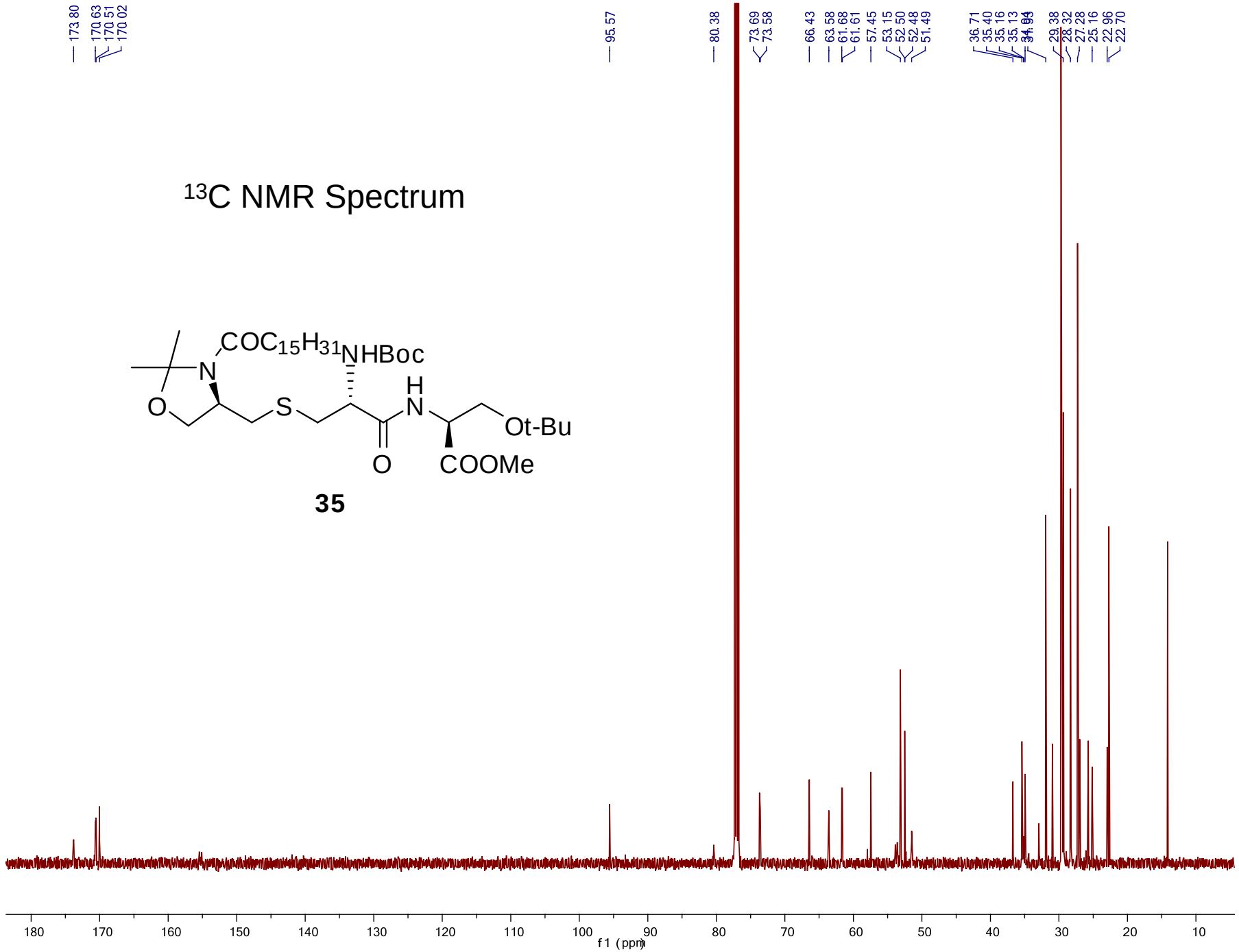

171.10
169.73
155.02
95.54
80.37
66.36
57.42
53.39
52.79
35.86
35.49
35.46
31.92
29.70
26.96
25.08
22.90
22.70
14.15
13C NMR Spectrum不
COC15H31
N
NHBoc
O
S
O
O
34
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


TOF Spectrum
Profile Spectrum at 11558.00 min (scan 1)
609.3883
686.51081
610.39142
687.51389
611.39066
688.51426
Abundance
400K
350K
300K
250K
200K
150K
100K
50K
0
500
600
700
800
900
1000
1100
m/z
COC15H31
N
O
S
NHBoc
O
O
34

^{1}H NMR Spectrum

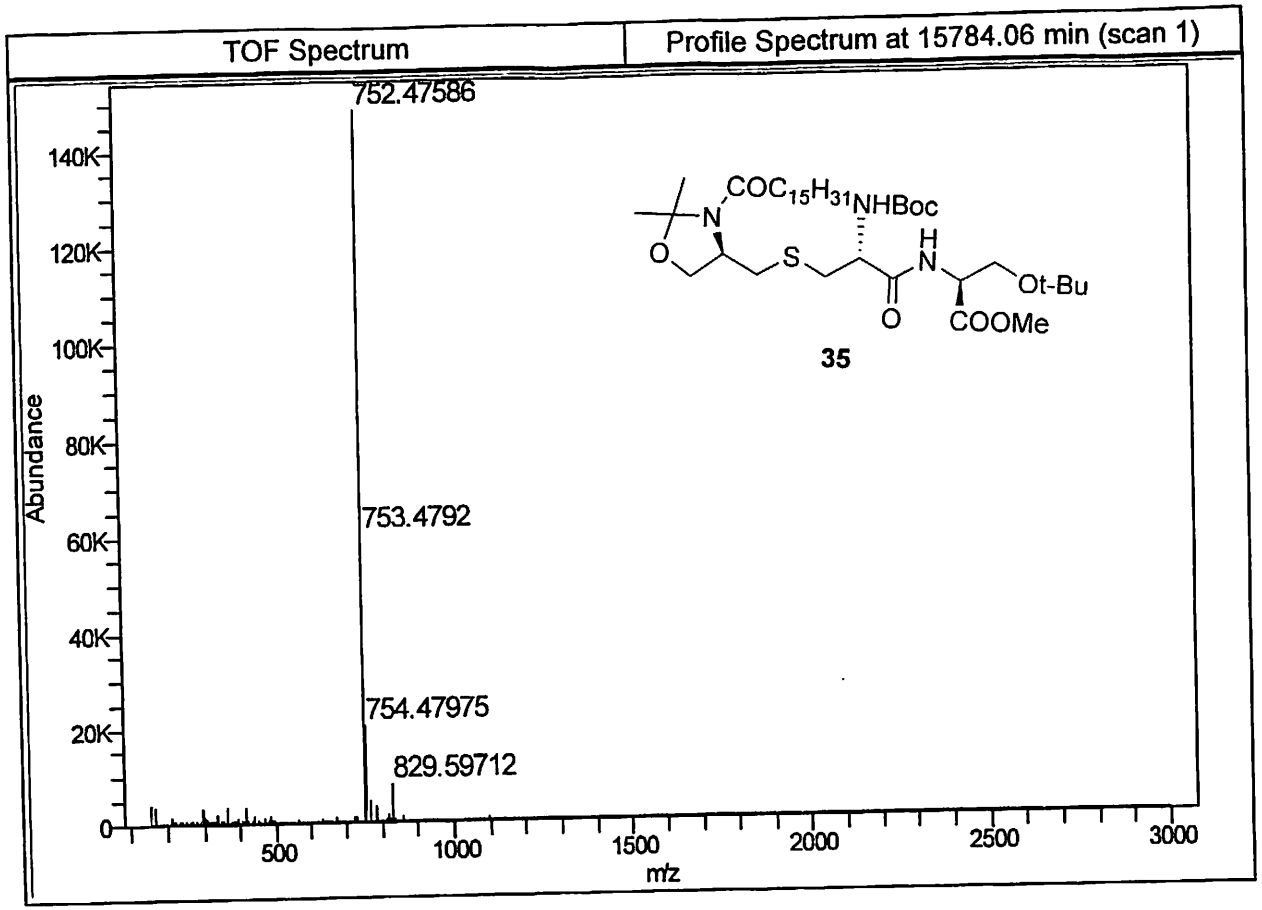
35





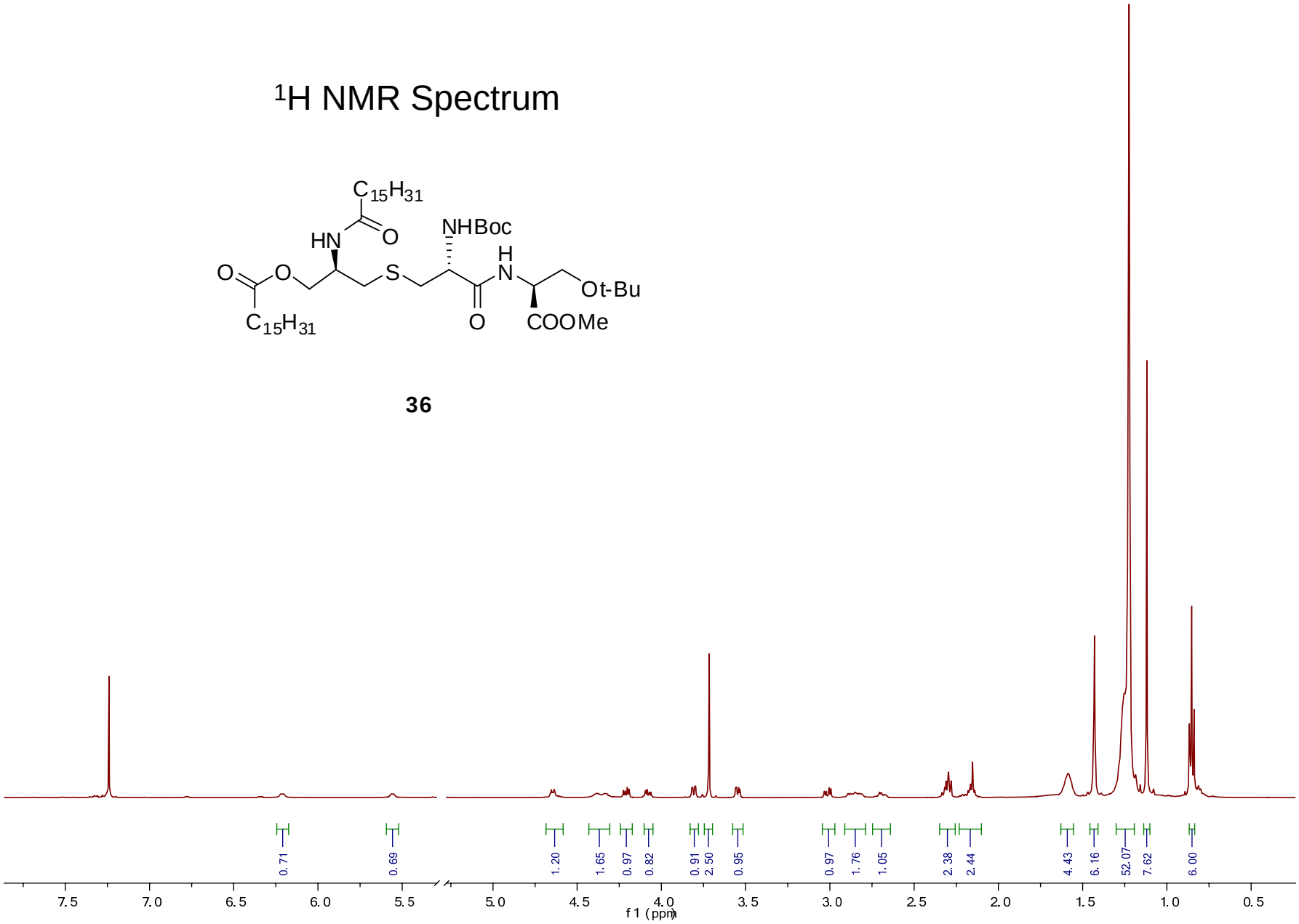
^{13}C NMR Spectrum

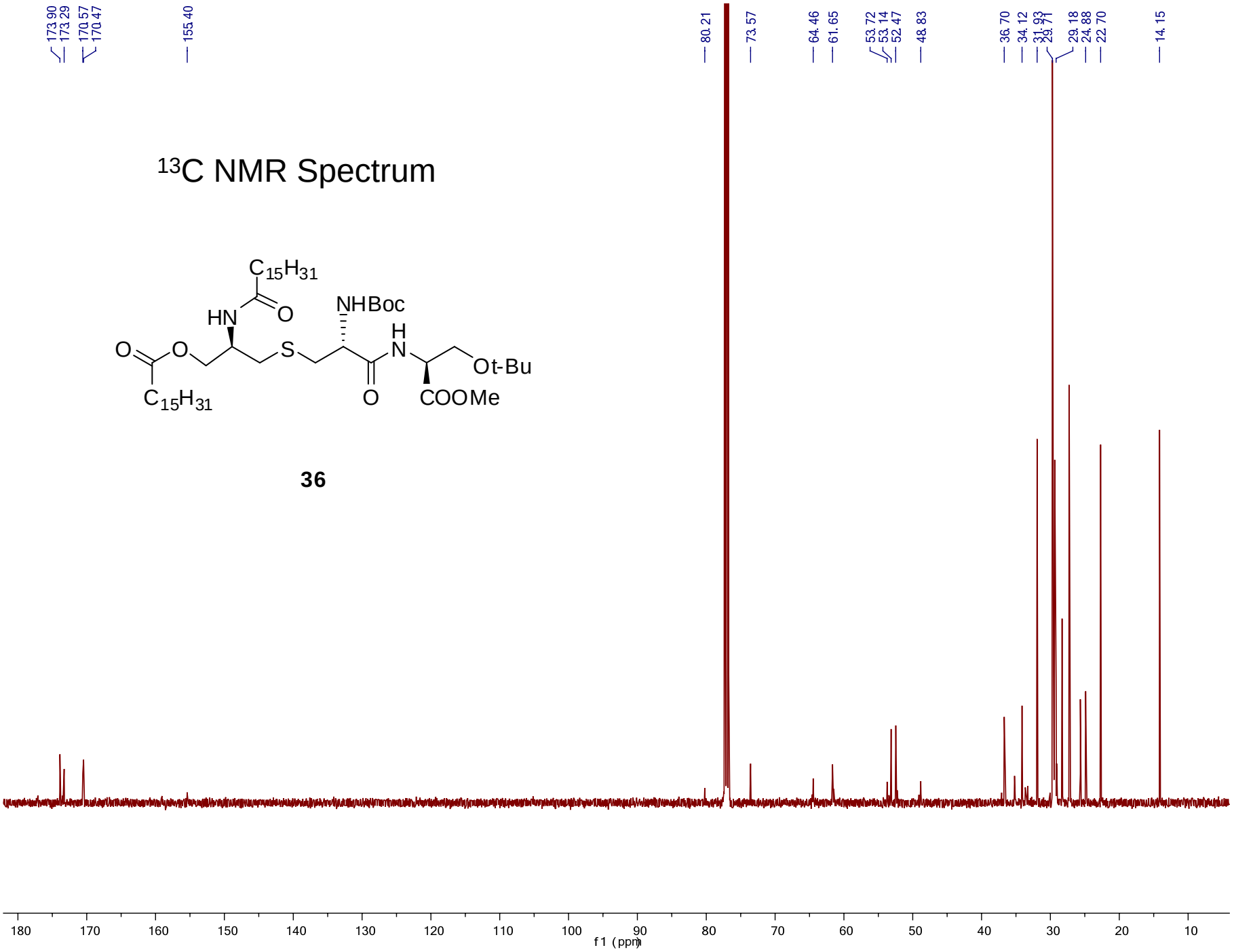
35

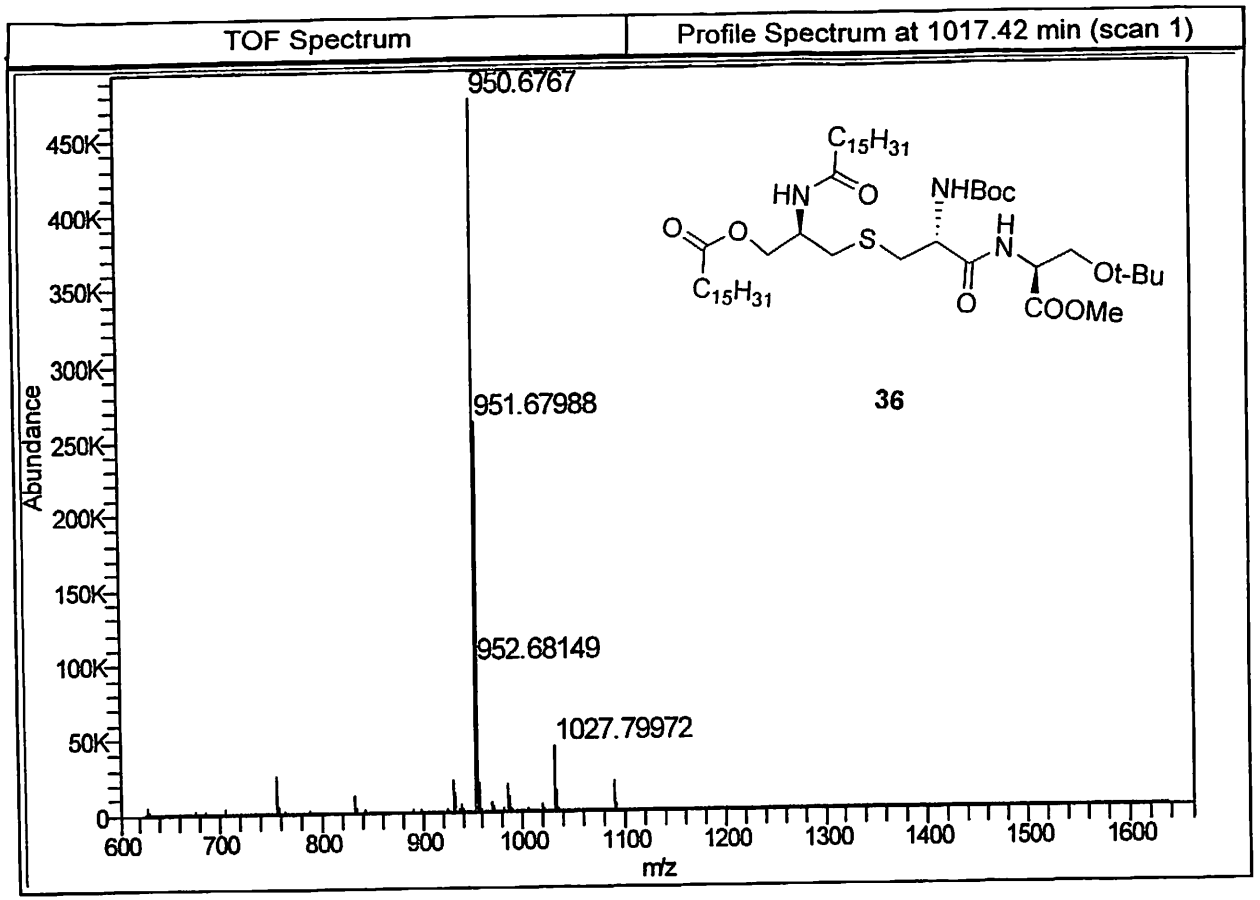

TOF Spectrum
Profile Spectrum at 15784.06 min (scan 1)
752.47586
753.4792
754.47975
829.59712
Abundance
m/z
140K
120K
100K
80K
60K
40K
20K
0
500
1000
1500
2000
2500
3000
COC15H31NHBoc
Ot-Bu
COOMe
35

^{1}H NMR Spectrum

36

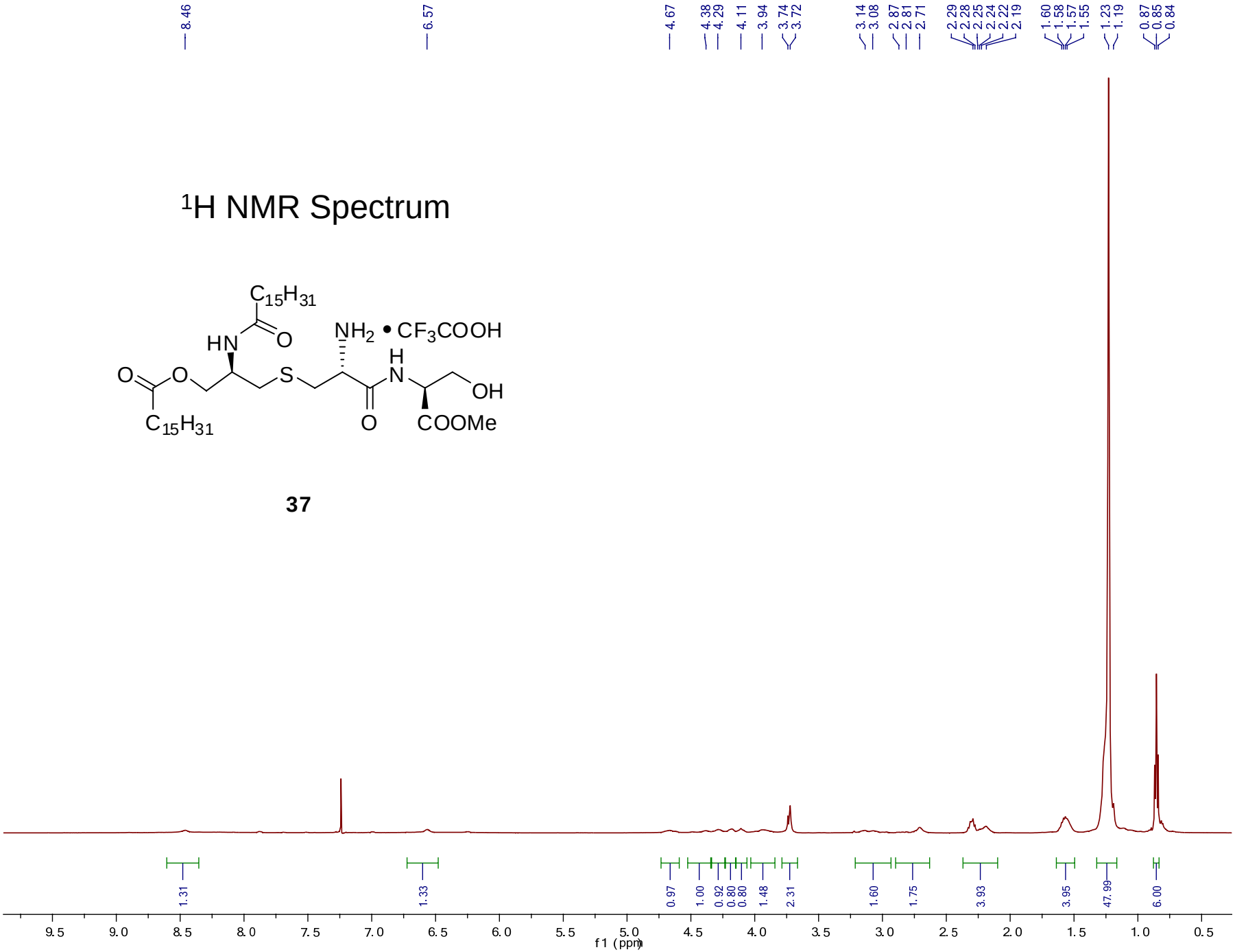



173.90
173.29
170.57
170.47
155.40
80.21
73.57
64.46
61.65
53.72
53.14
52.47
48.83
36.70
34.12
31.93
29.71
29.18
24.88
22.70
14.15
13C NMR Spectrum
C15H31
HN
O
NHBoc
O
O
S
H
N
Ot-Bu
C15H31
O
COOMe
36
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


TOF Spectrum
Profile Spectrum at 1017.42 min (scan 1)
950.6767
951.67988
952.68149
1027.79972
Abundance
m/z
450K
400K
350K
300K
250K
200K
150K
100K
50K
0
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
C15H31
HN
O
NHBoc
O
O
S
H
N
Ot-Bu
C15H31
O
COOMe
36

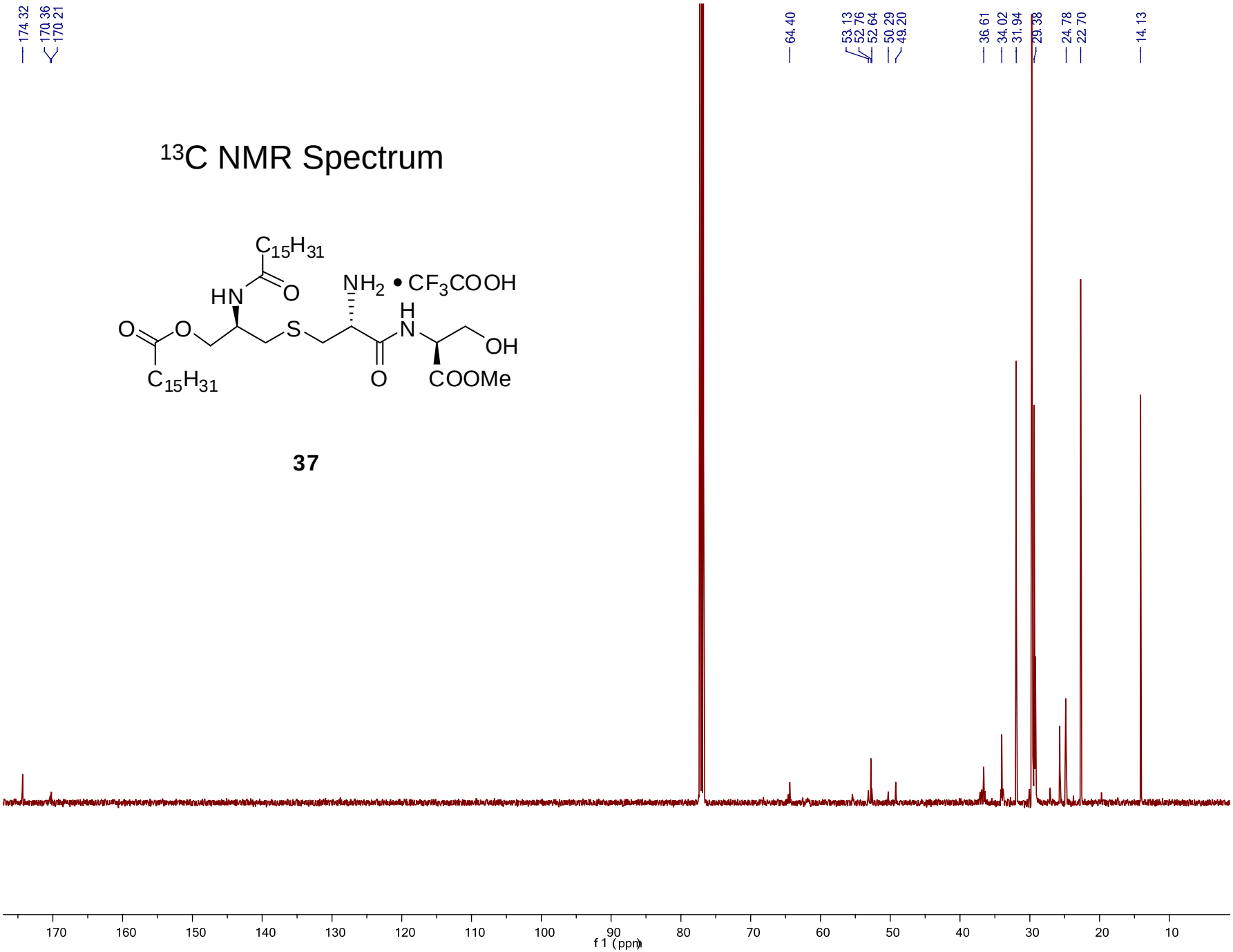
^{1}H NMR Spectrum

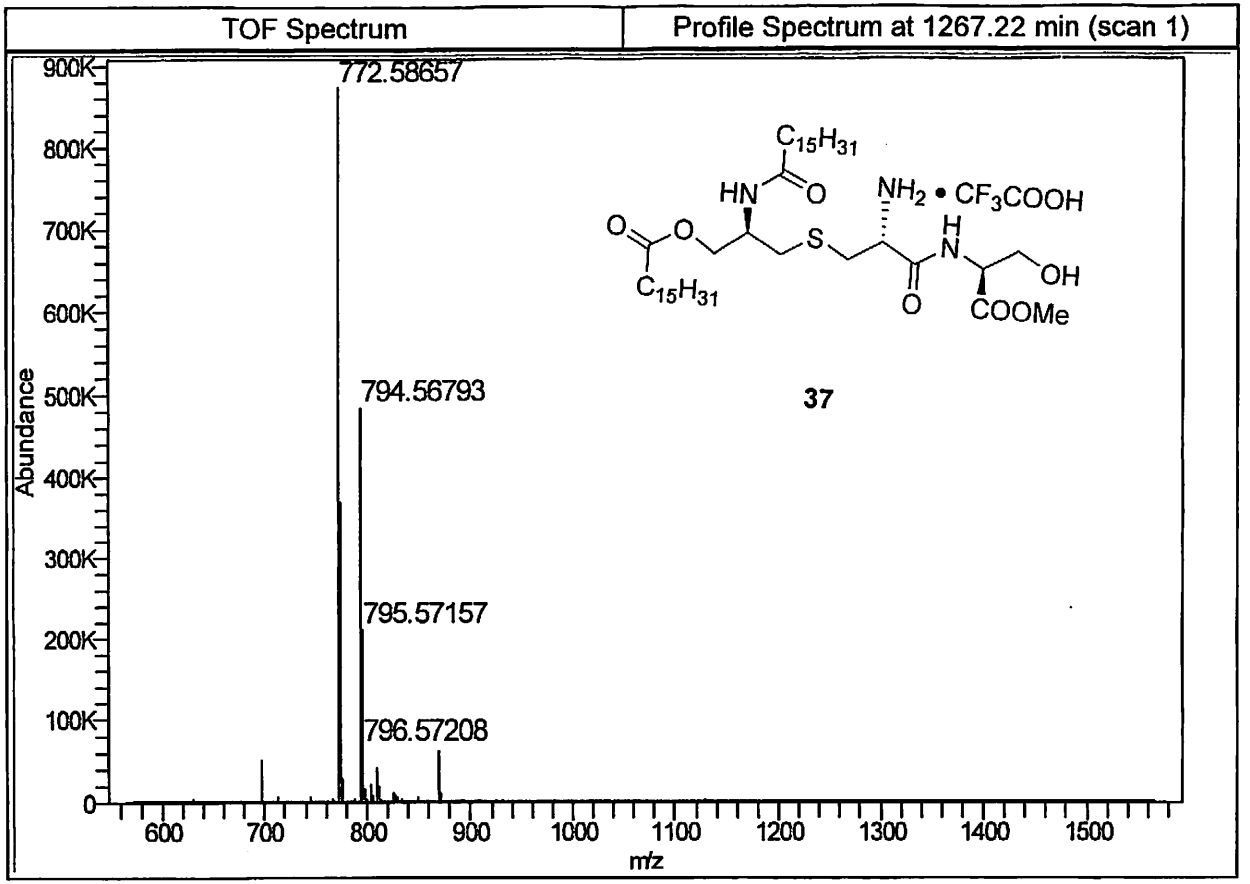
37



^{13}C NMR Spectrum

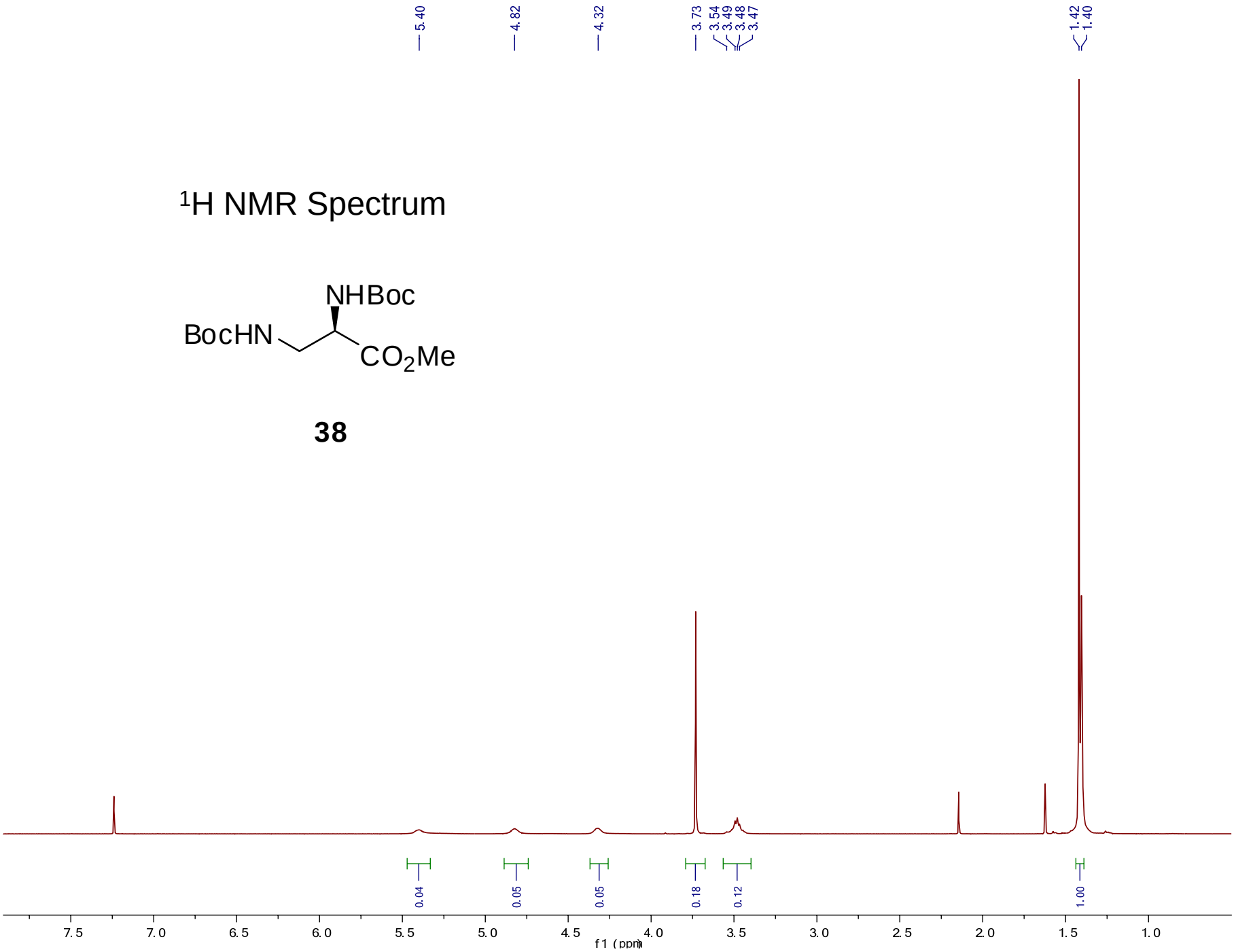
37

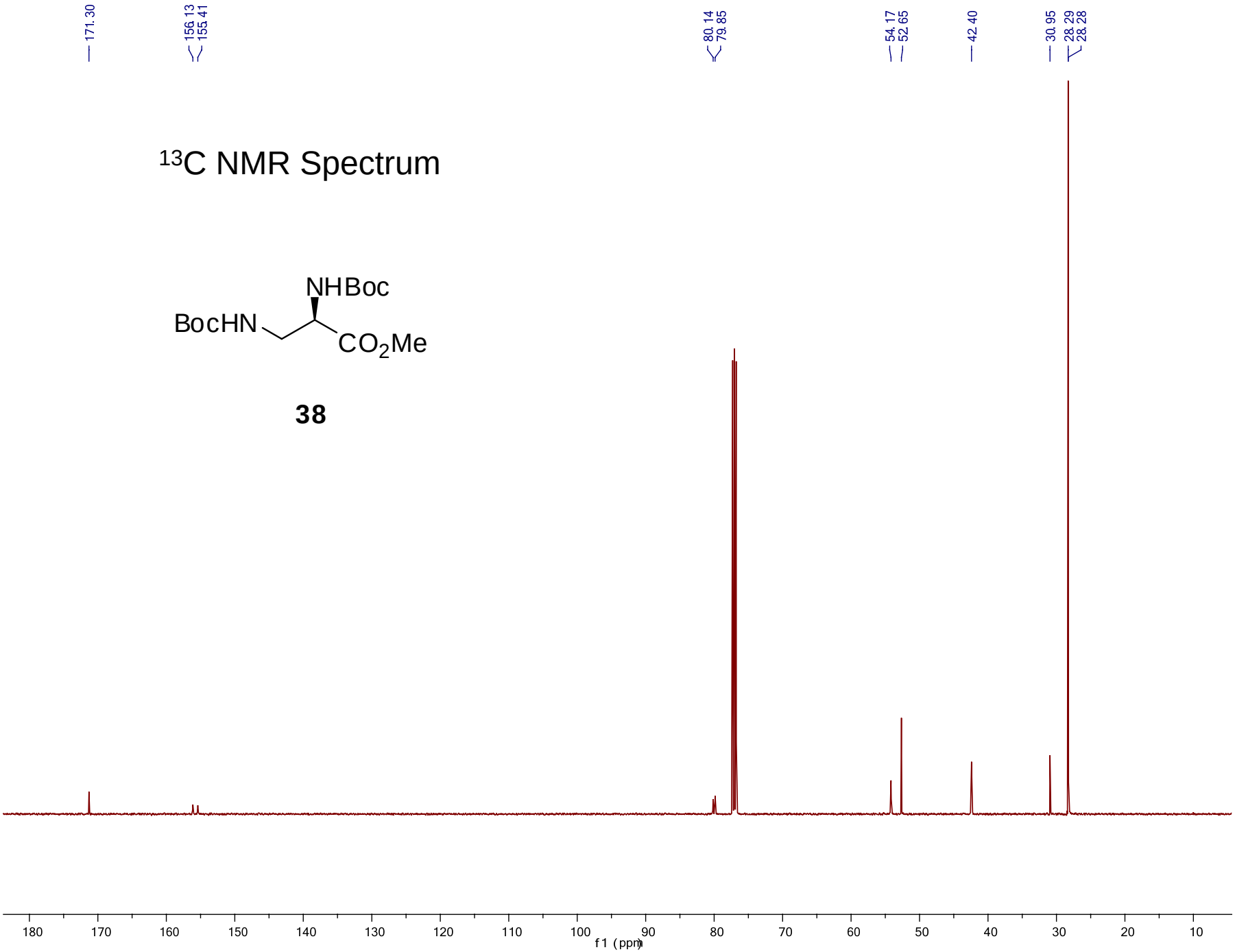


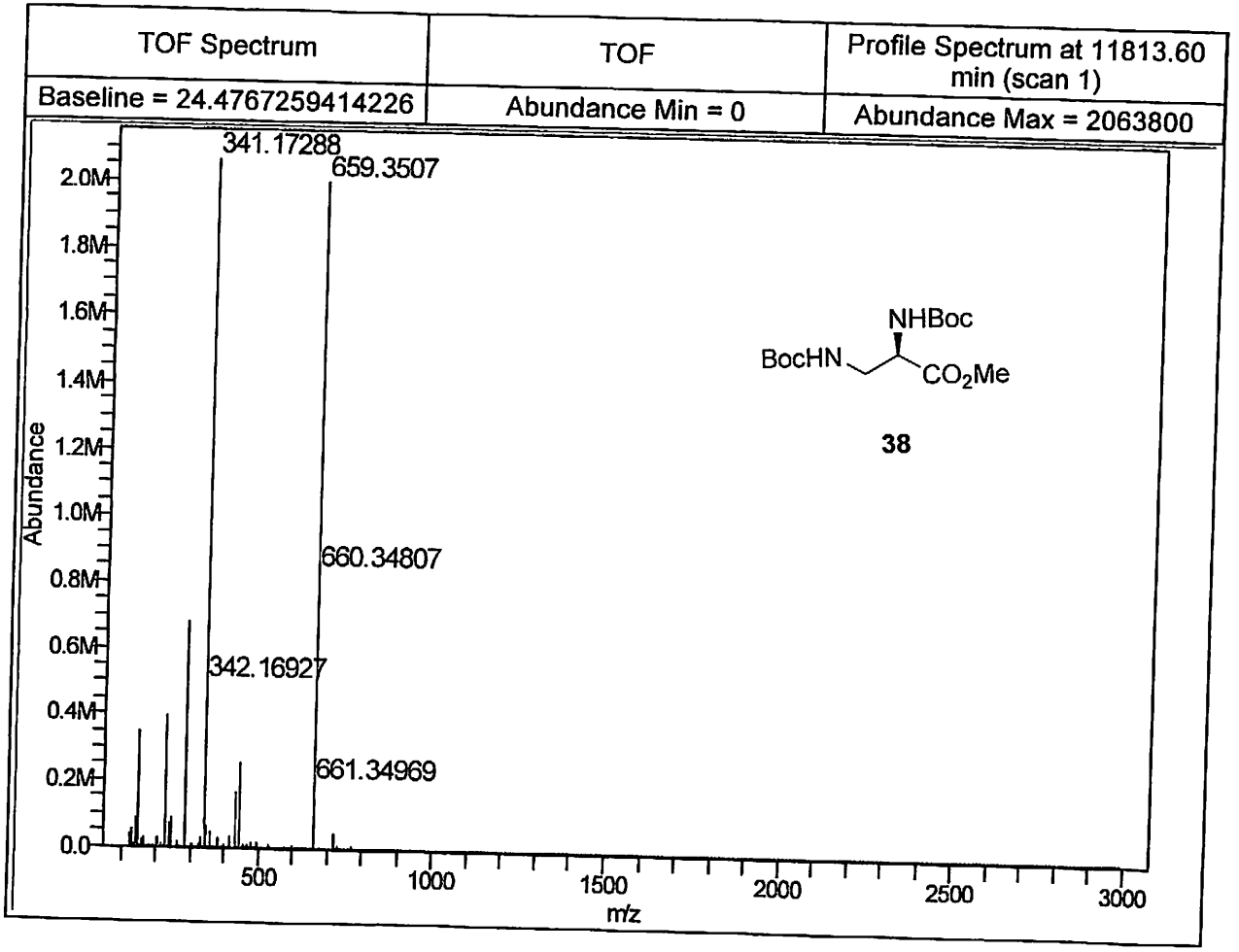

TOF Spectrum
Profile Spectrum at 1267.22 min (scan 1)
772.58657
794.56793
795.57157
796.57208
Abundance
m/z
900K
800K
700K
600K
500K
400K
300K
200K
100K
0
600
700
800
900
1000
1100
1200
1300
1400
1500
$C_{15}H_{31}$
HN
O
$NH_2 \bullet CF_3COOH$
O
O
S
H
N
OH
$C_{15}H_{31}$
O
COOMe
37

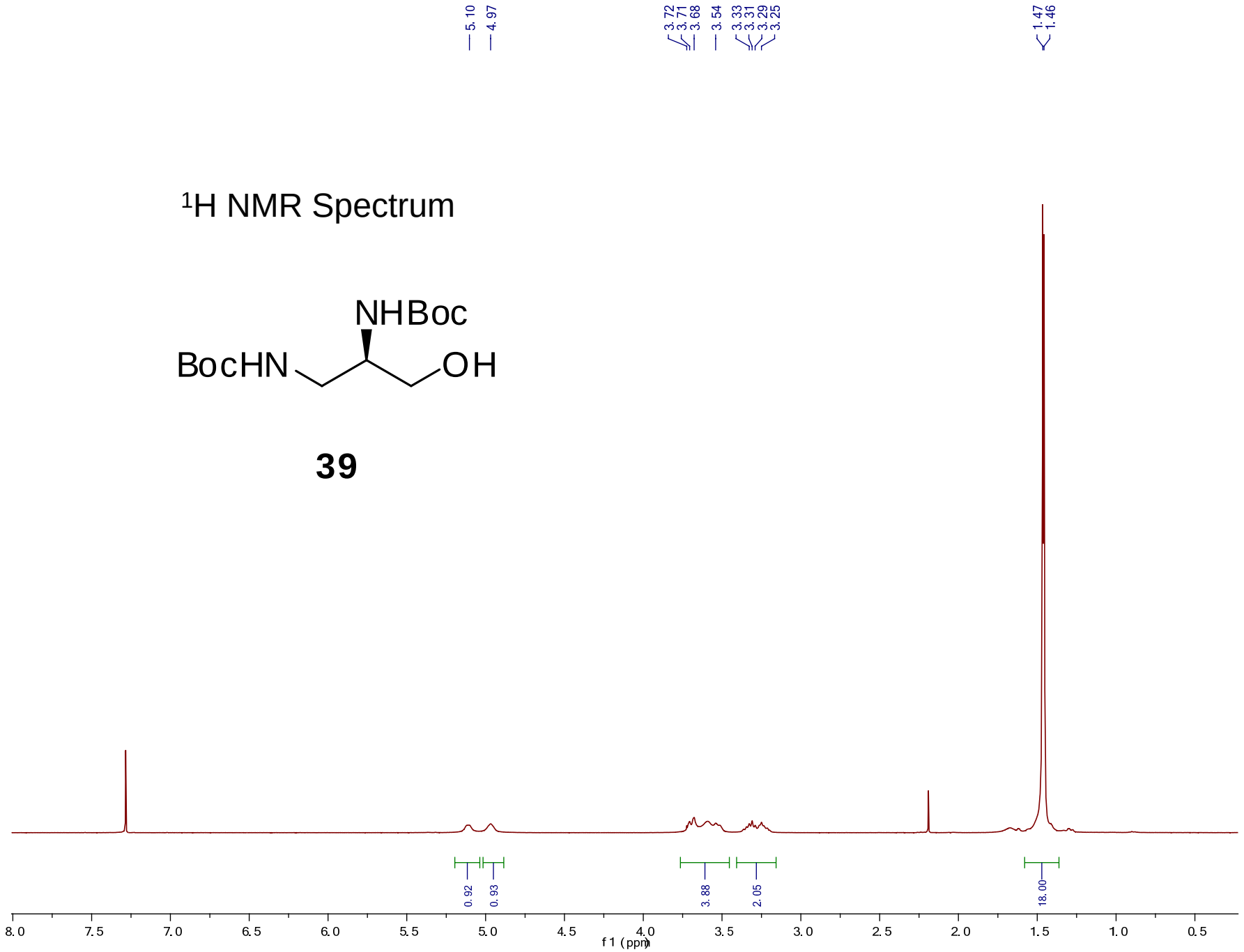
^{1}H NMR Spectrum

38



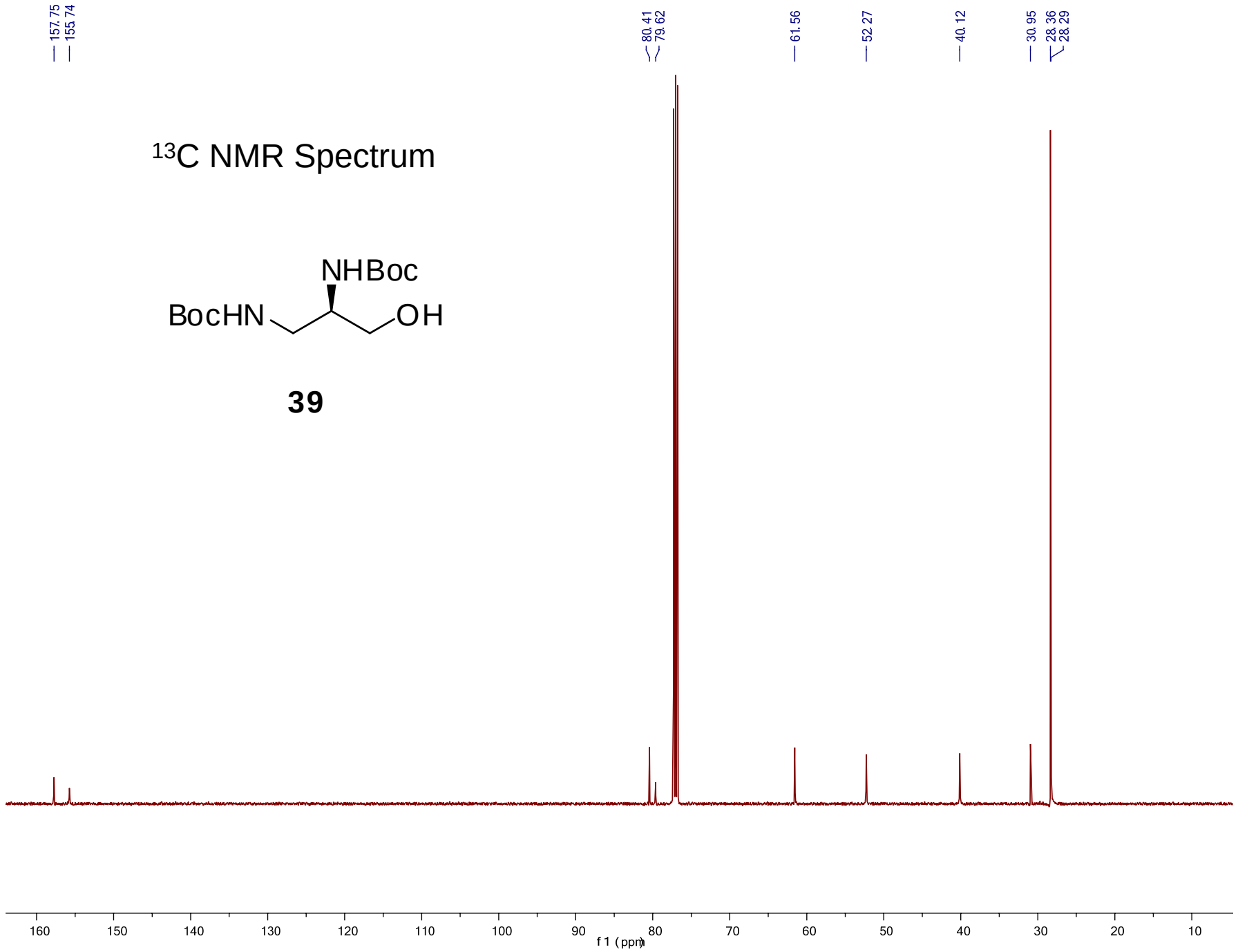

171.30
156.13
155.41
80.14
79.85
54.17
52.65
42.40
30.95
28.29
28.28
13C NMR Spectrum
NHBoc
BocHN
CO2Me
38
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

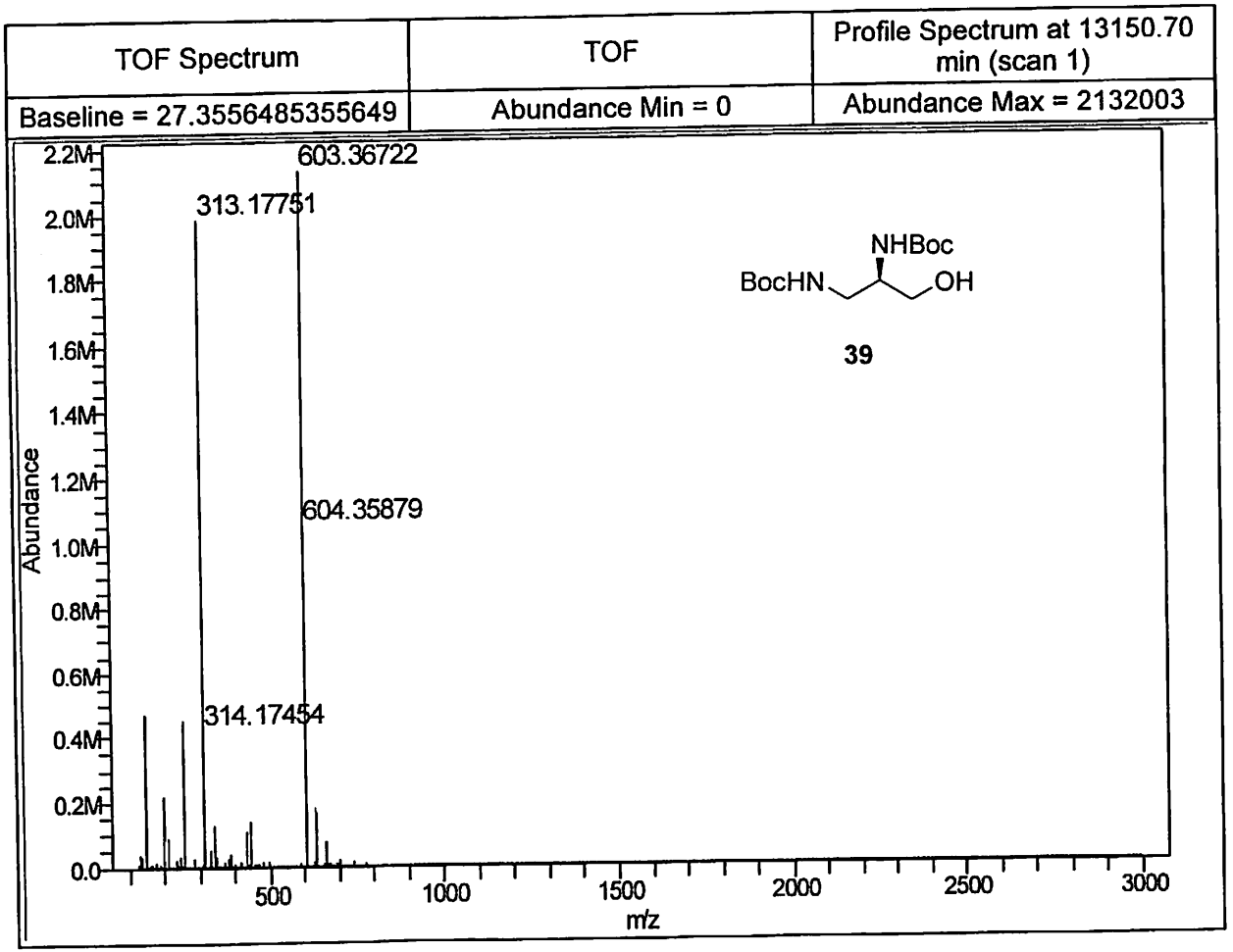

TOF Spectrum
TOF
Profile Spectrum at 11813.60 min (scan 1)
Baseline = 24.4767259414226
Abundance Min = 0
Abundance Max = 2063800
341.17288
659.3507
660.34807
342.16927
661.34969
Abundance
2.0M
1.8M
1.6M
1.4M
1.2M
1.0M
0.8M
0.6M
0.4M
0.2M
0.0
500
1000
1500
2000
2500
3000
m/z
NHBoc
BocHN
CO2Me
38

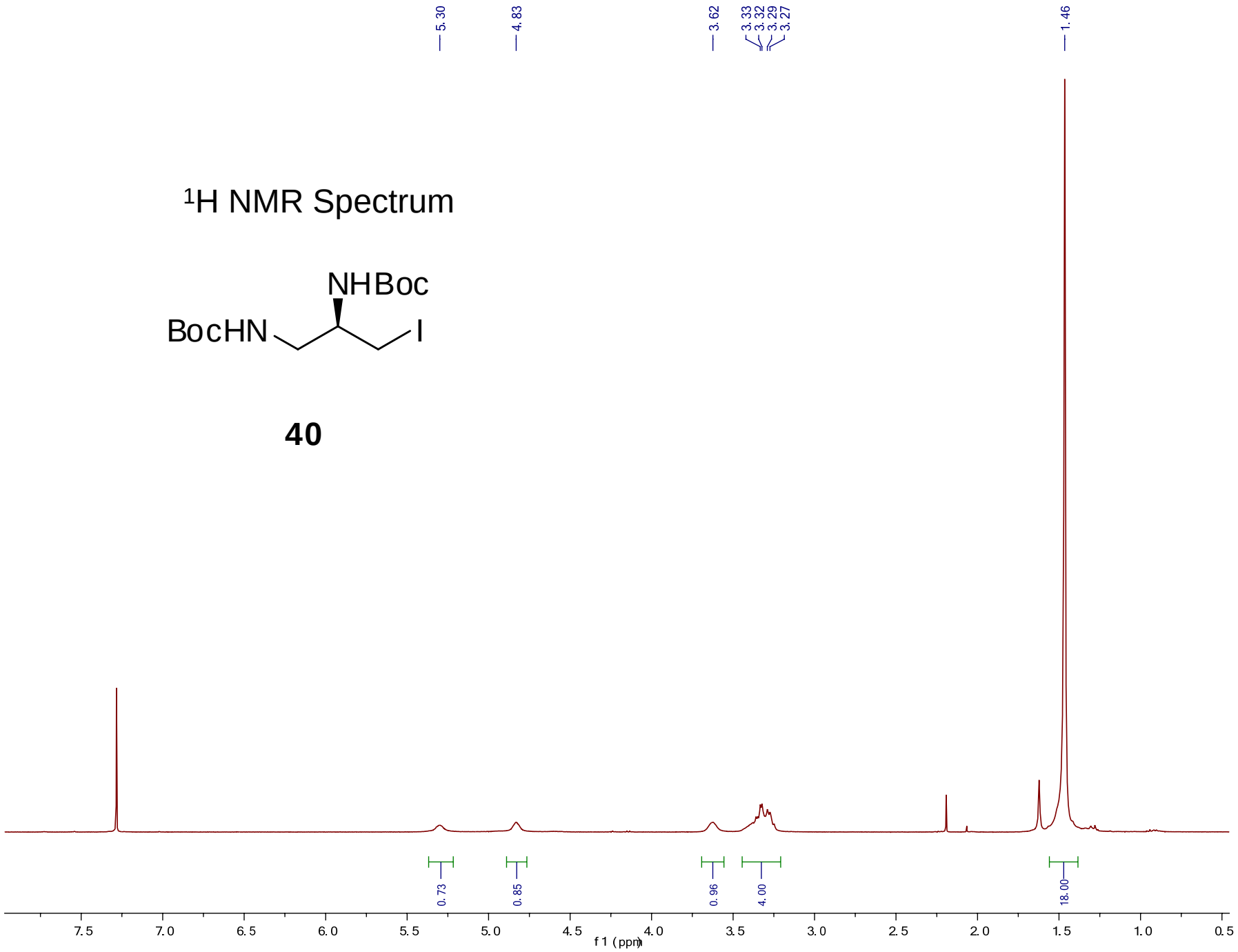


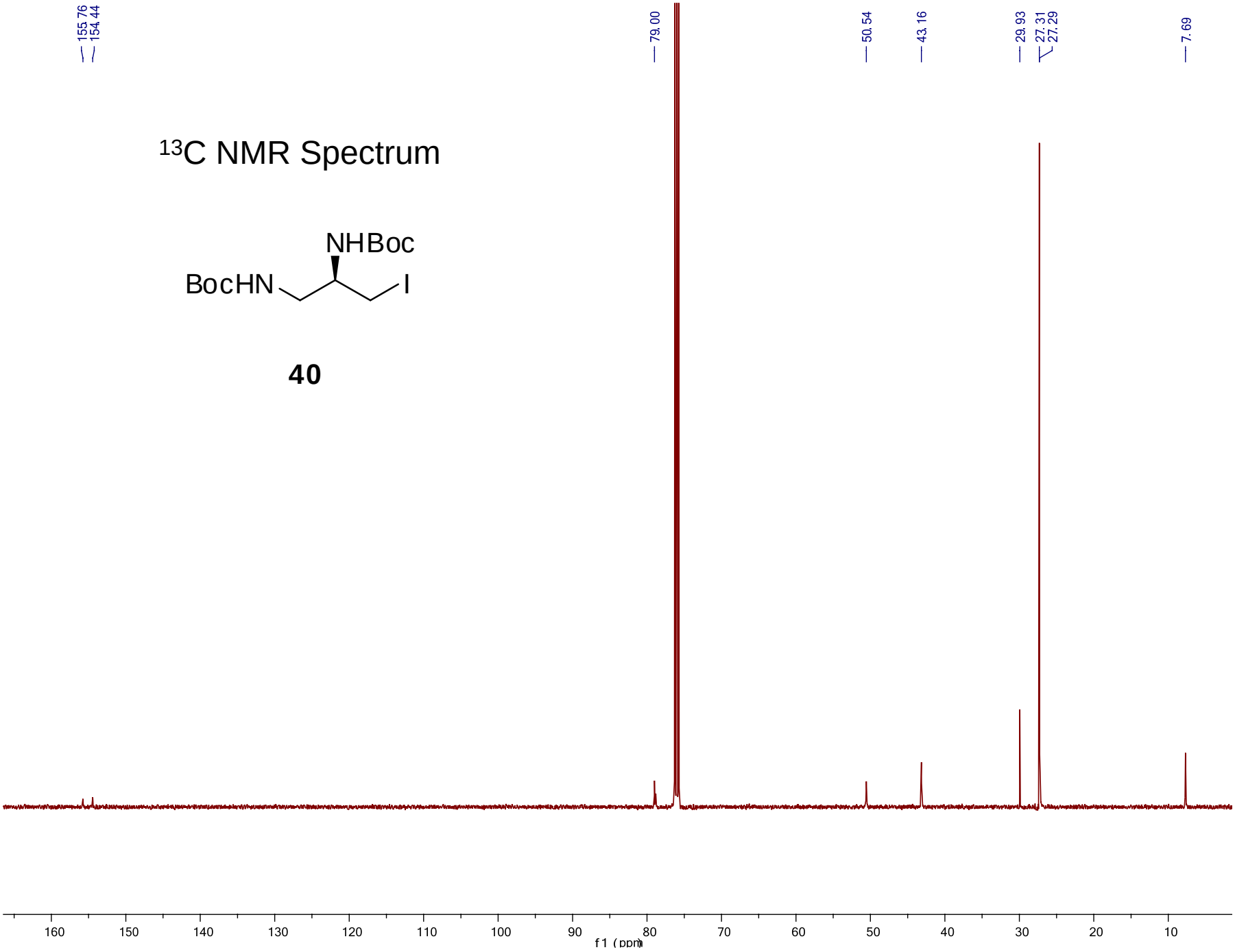
^{1}H NMR Spectrum

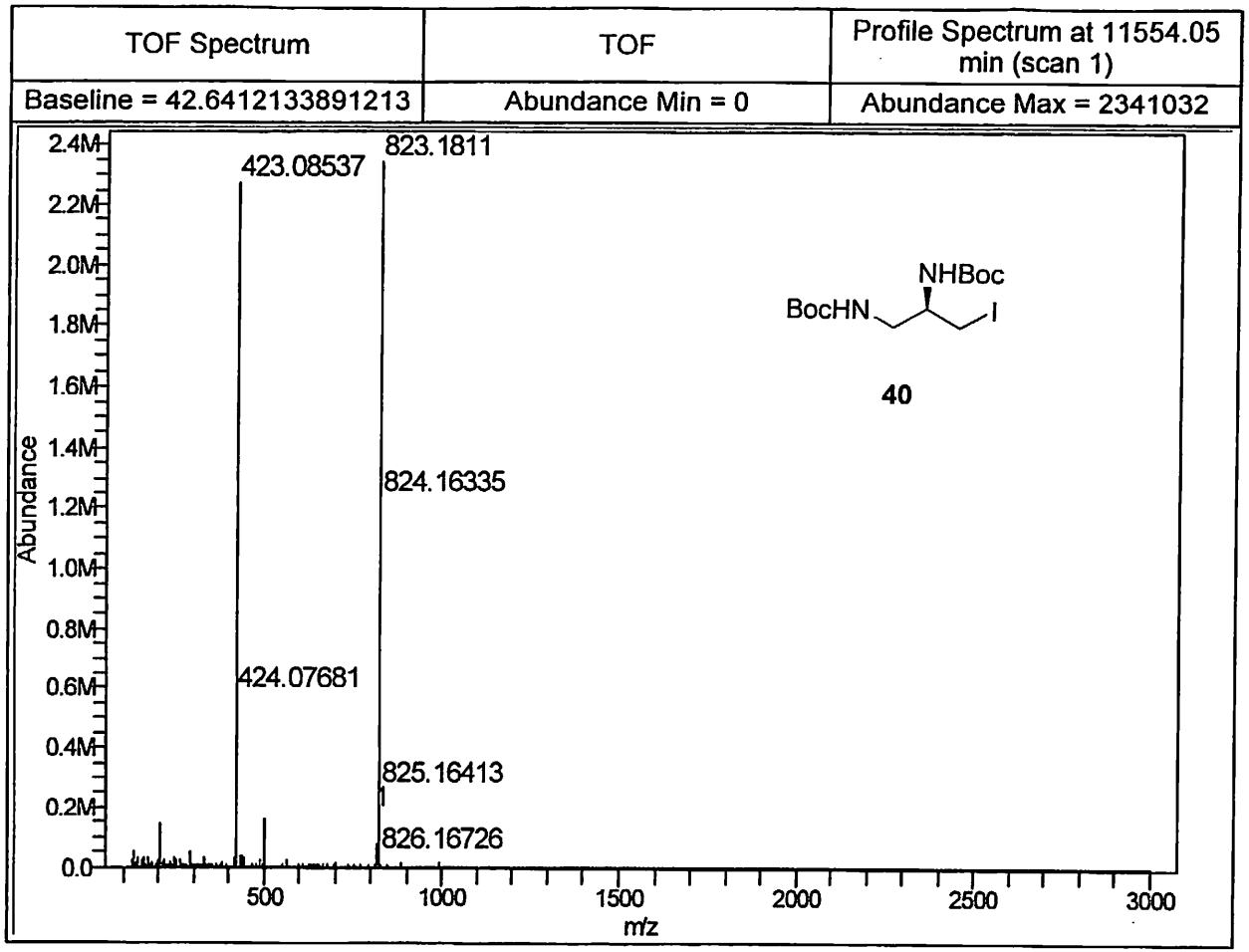
39


157.75
155.74
80.41
79.62
61.56
52.27
40.12
30.95
28.36
28.29
13C NMR Spectrum
NHBoc
BocHN
OH
39
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


TOF Spectrum
TOF
Profile Spectrum at 13150.70 min (scan 1)
Baseline = 27.3556485355649
Abundance Min = 0
Abundance Max = 2132003
603.36722
313.17751
604.35879
314.17454
Abundance
2.2M
2.0M
1.8M
1.6M
1.4M
1.2M
1.0M
0.8M
0.6M
0.4M
0.2M
0.0
500
1000
1500
2000
2500
3000
m/z
NHBoc
BocHN
OH
39


5.30
4.83
3.62
3.33
3.32
3.29
3.27
1.46
^{1}H NMR Spectrum
NHBoc
BocHN
I
40
0.73
0.85
0.96
4.00
18.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

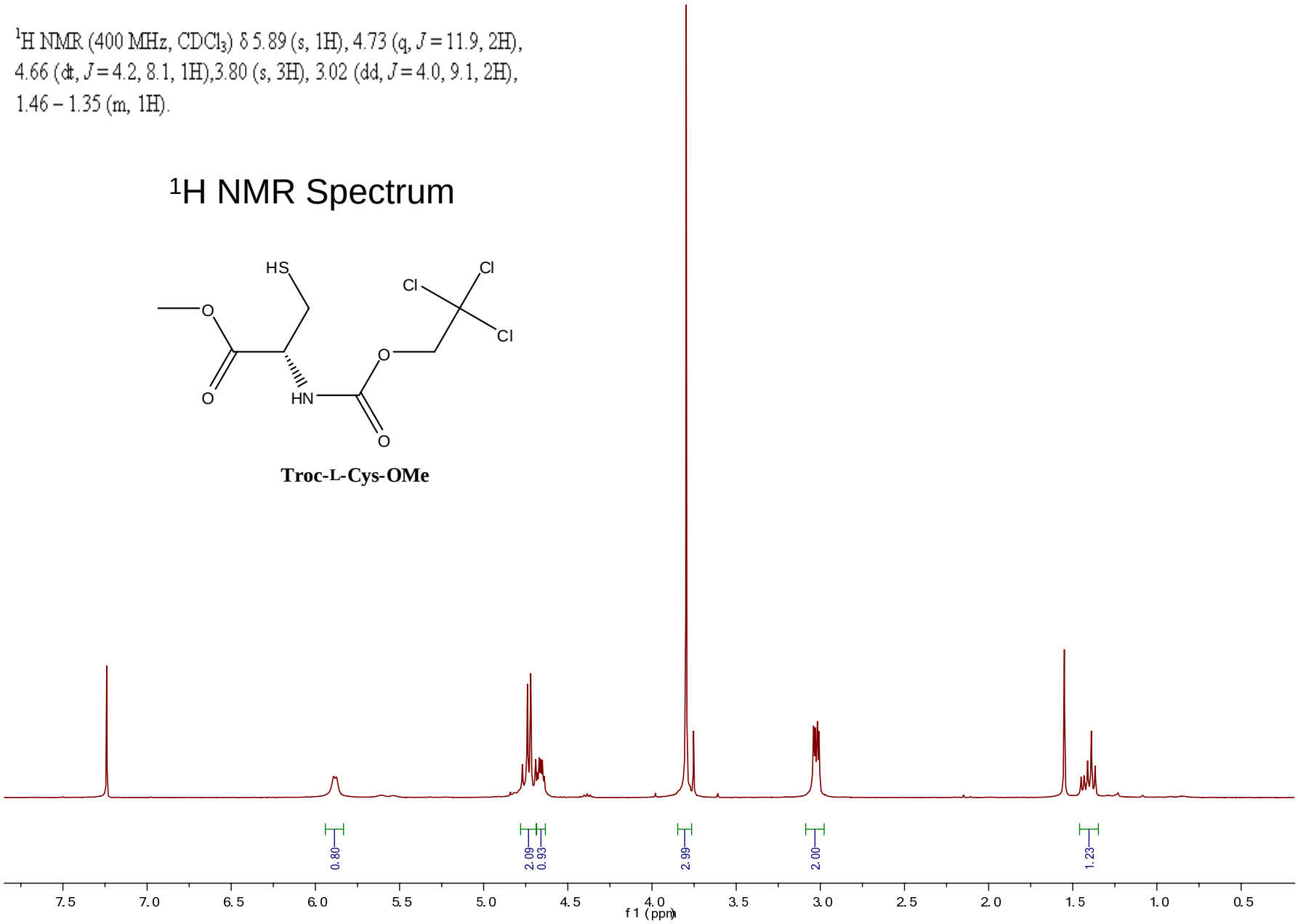

155.76
154.44
79.00
50.54
43.16
29.93
27.31
27.29
7.69
13C NMR Spectrum
NHBoc
BocHN
I
40
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

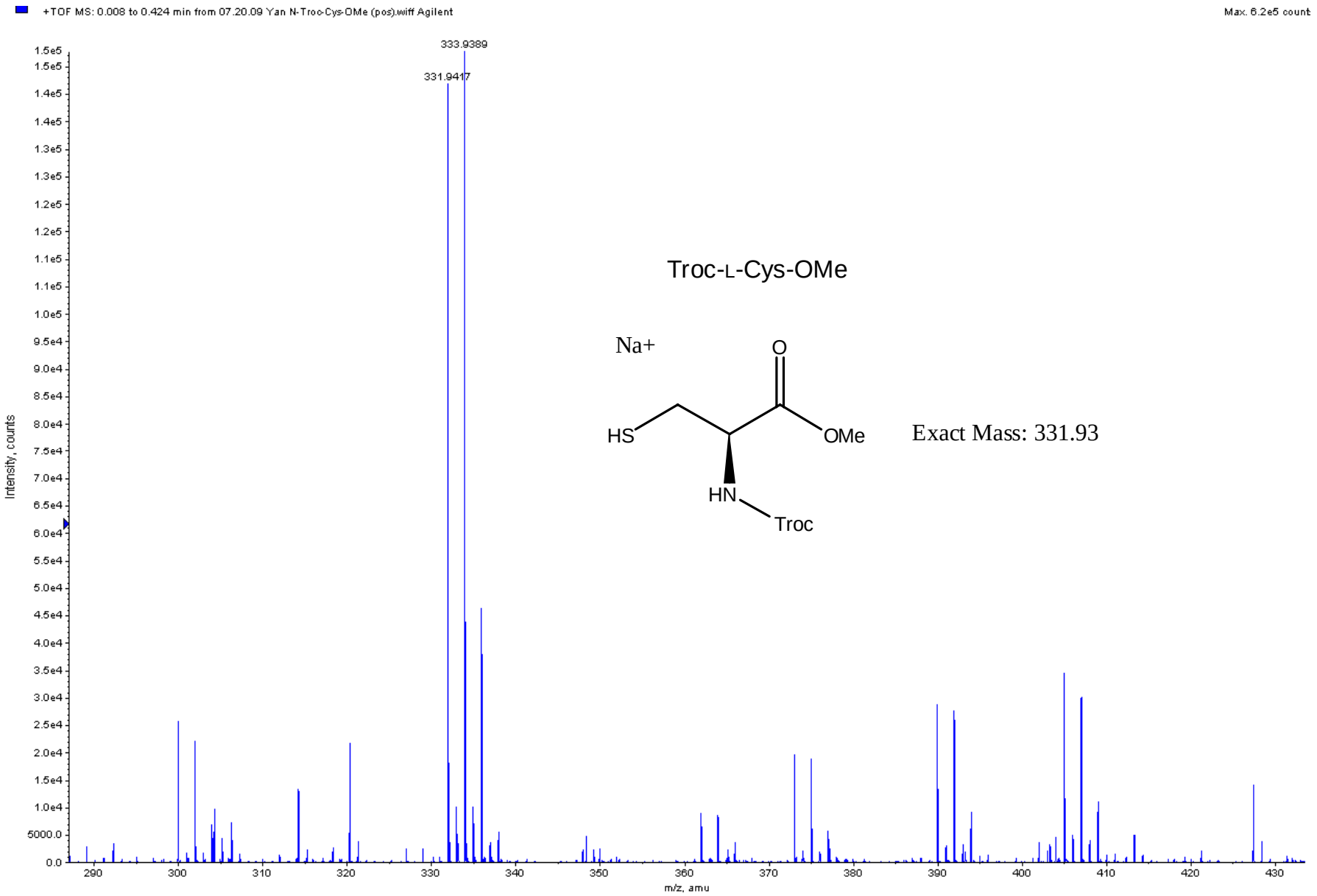

TOF Spectrum
TOF
Profile Spectrum at 11554.05 min (scan 1)
Baseline = 42.6412133891213
Abundance Min = 0
Abundance Max = 2341032
Abundance
m/z
423.08537
823.1811
824.16335
424.07681
825.16413
826.16726
NHBoc
BocHN
I
40

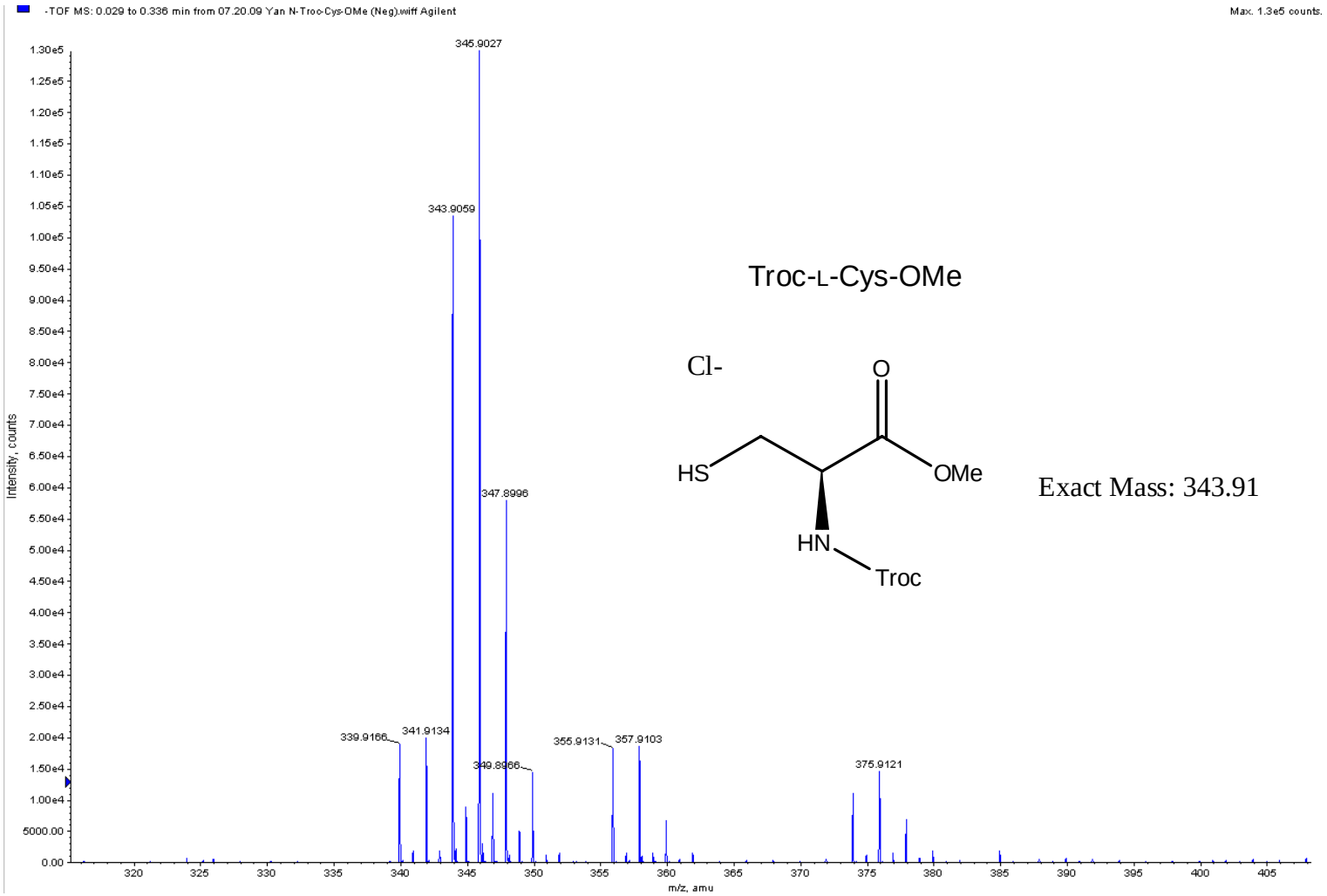
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 (s, 1H), 4.73 (q, J = 11.9, 2H), 4.66 (dt, J = 4.2, 8.1, 1H),3.80 (s, 3H), 3.02 (dd, J = 4.0, 9.1, 2H), 1.46 – 1.35 (m, 1H).

^{1}H NMR Spectrum

Troc-L-Cys-OMe

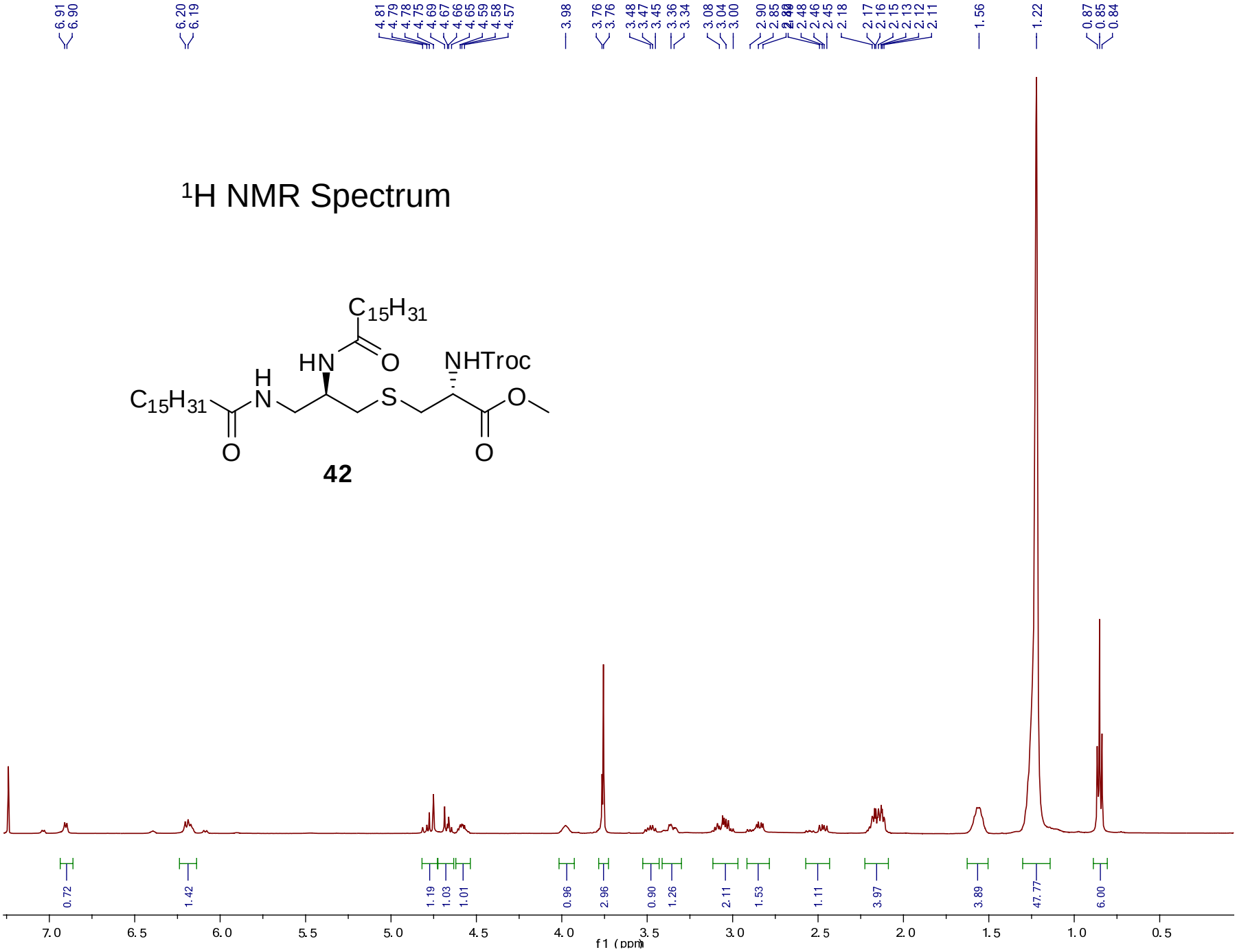


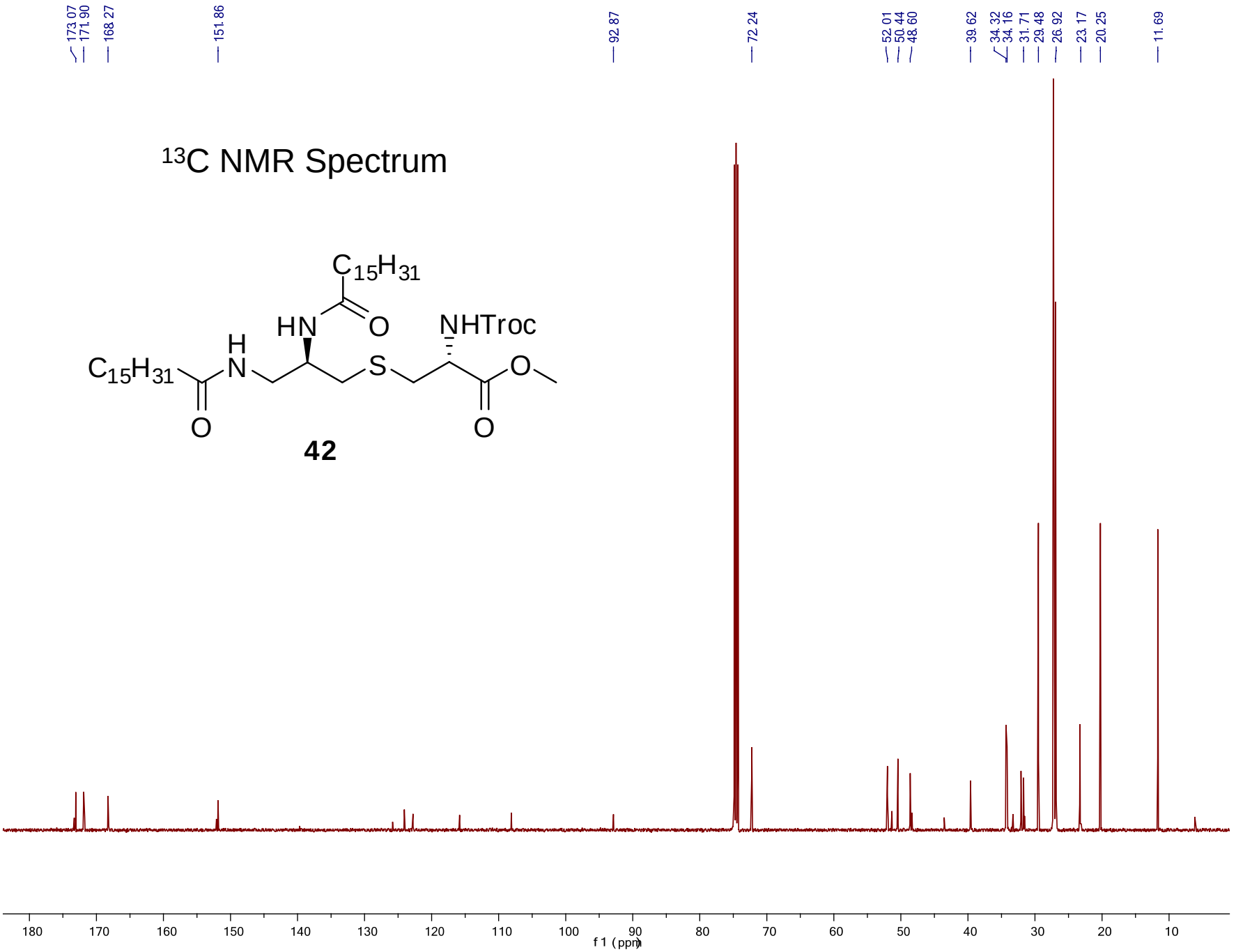

+TOF MS: 0.008 to 0.424 min from 07.20.09 Yan N-Troc-Cys-OMe (pos).wiff Agilent
Max. 6.2e5 count
333.9389
331.9417
Intensity, counts
m/z, amu
Troc-L-Cys-OMe
Na+
O
HS
OMe
HN
Troc
Exact Mass: 331.93

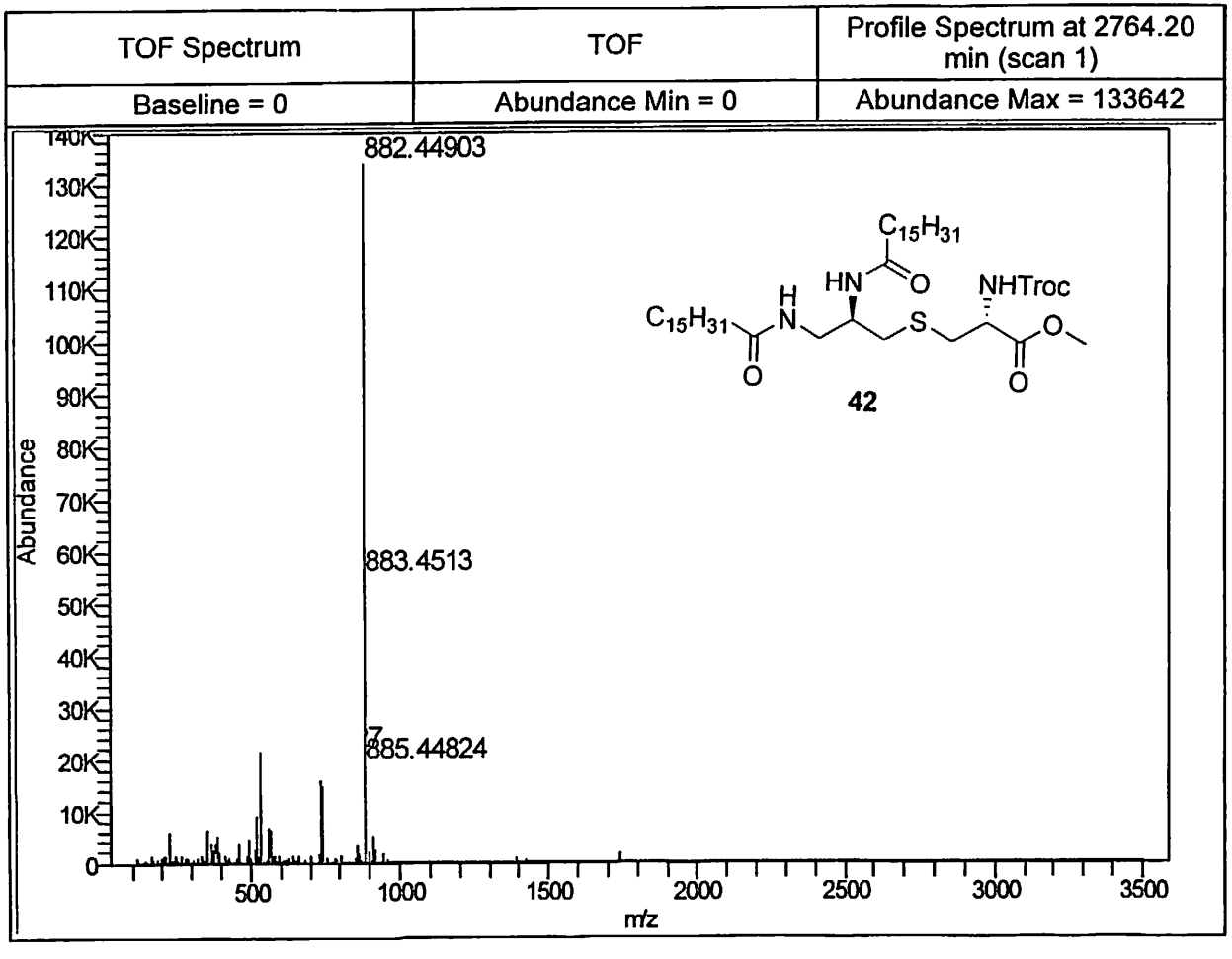

-TOF MS: 0.029 to 0.336 min from 07.20.09 Yan N-Troc-Cys-OMe (Neg).wiff Agilent
Max. 1.3e5 counts.
Intensity, counts
m/z, amu
345.9027
343.9059
347.8996
339.9166
341.9134
349.8966
355.9131
357.9103
375.9121
Troc-L-Cys-OMe
Cl-
O
HS
OMe
HN
Troc
Exact Mass: 343.91

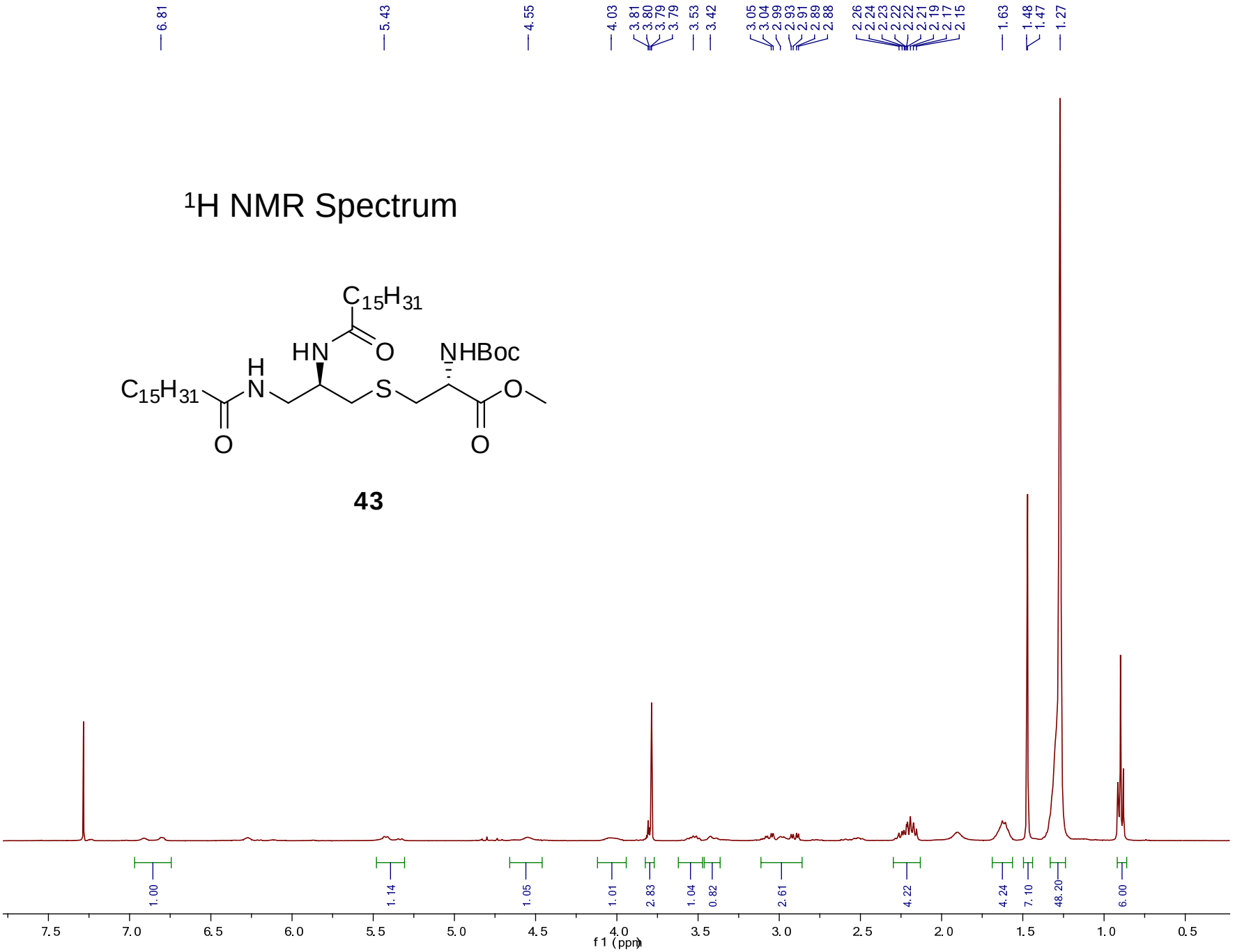
^{1}H NMR Spectrum

42




173.07
171.90
168.27
151.86
92.87
72.24
52.01
50.44
48.60
39.62
34.32
34.16
31.71
29.48
26.92
23.17
20.25
11.69
13C NMR Spectrum
C15H31
HN
O
NHTroc
H
N
C15H31
S
O
O
O
42
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


TOF Spectrum
TOF
Profile Spectrum at 2764.20 min (scan 1)
Baseline = 0
Abundance Min = 0
Abundance Max = 133642
882.44903
883.4513
885.44824
Abundance
m/z
140K
130K
120K
110K
100K
90K
80K
70K
60K
50K
40K
30K
20K
10K
0
500
1000
1500
2000
2500
3000
3500
C15H31
HN
O
NHTroc
H
N
S
O
O
O
42

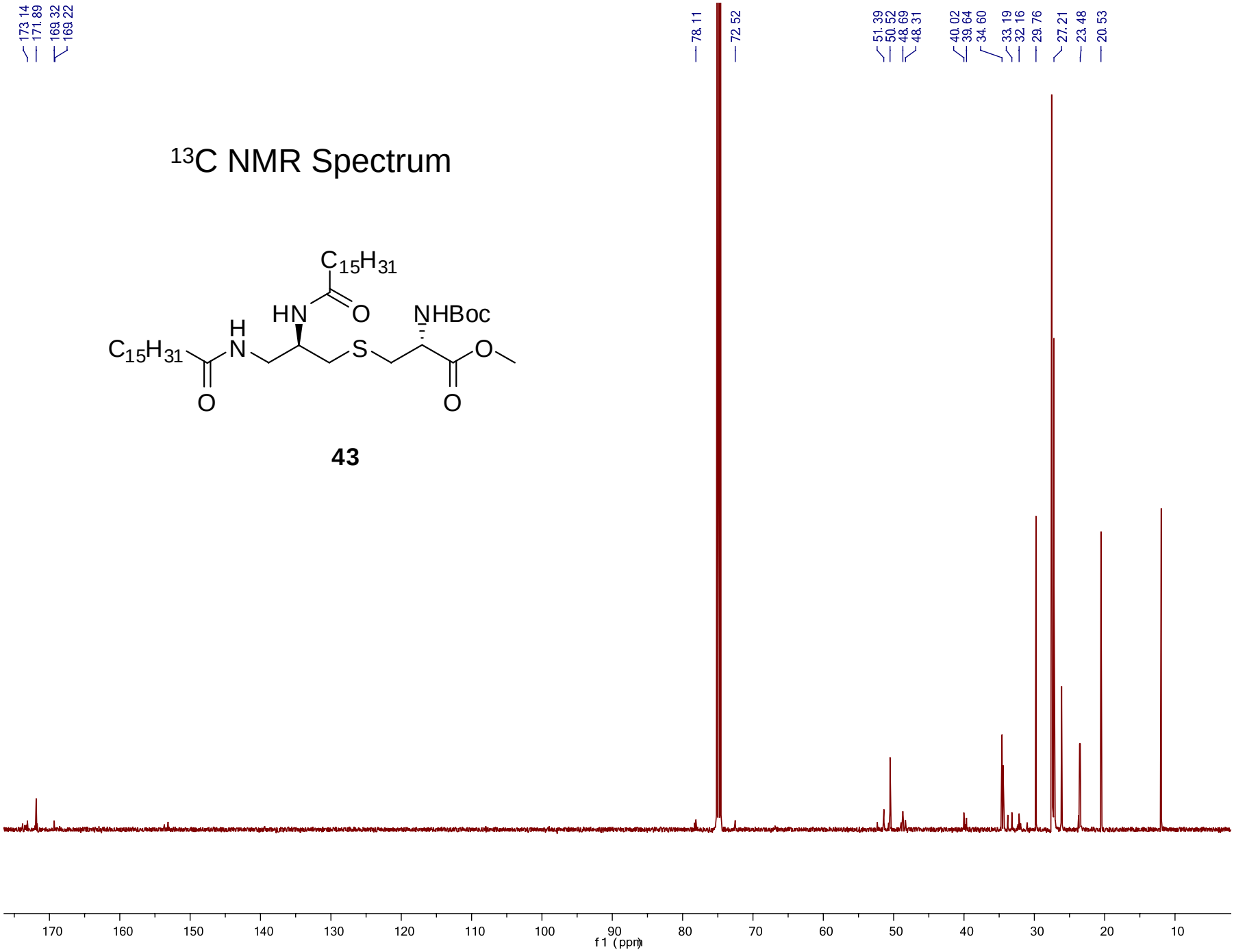


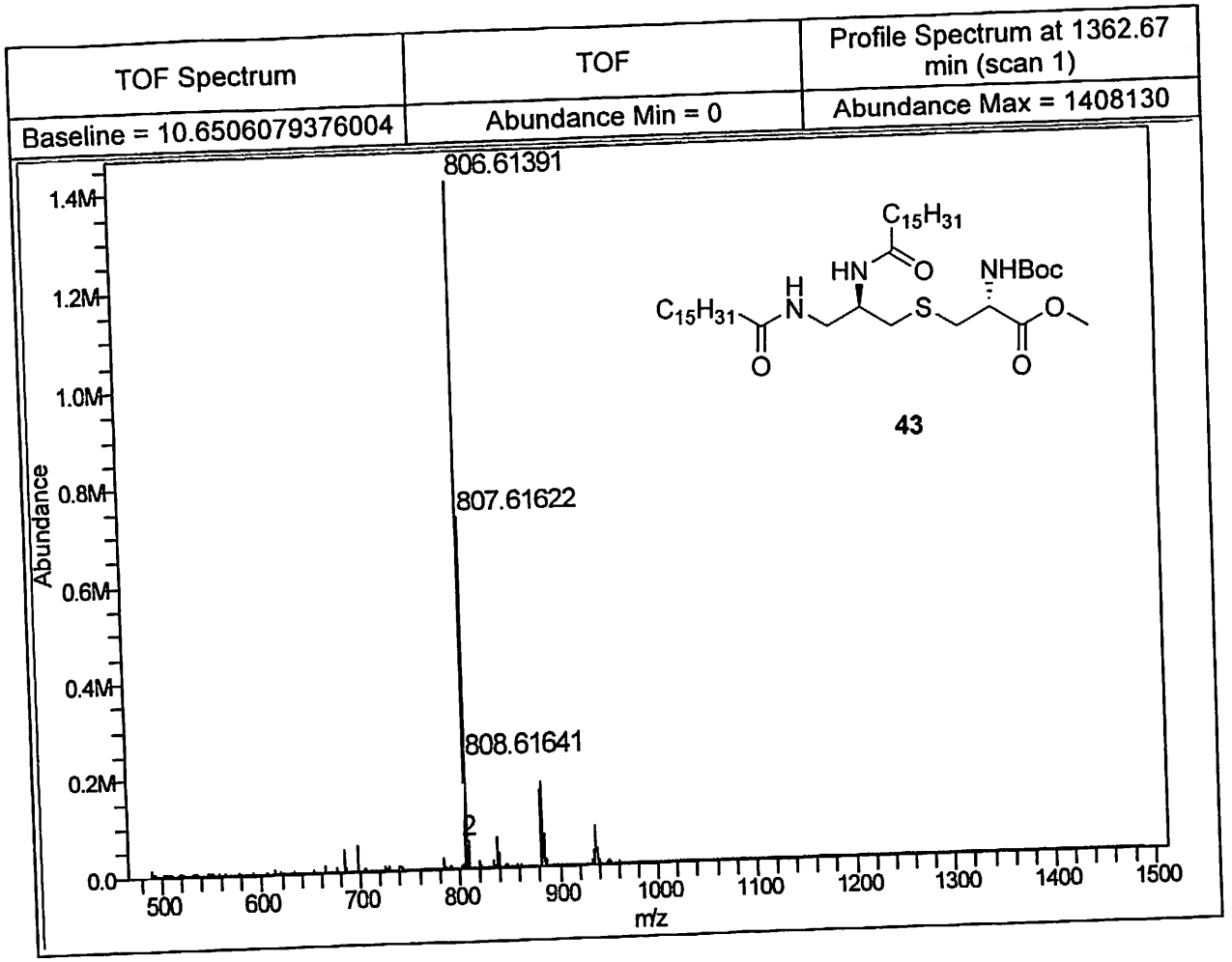
^{1}H NMR Spectrum

43

^{13}C NMR Spectrum

43

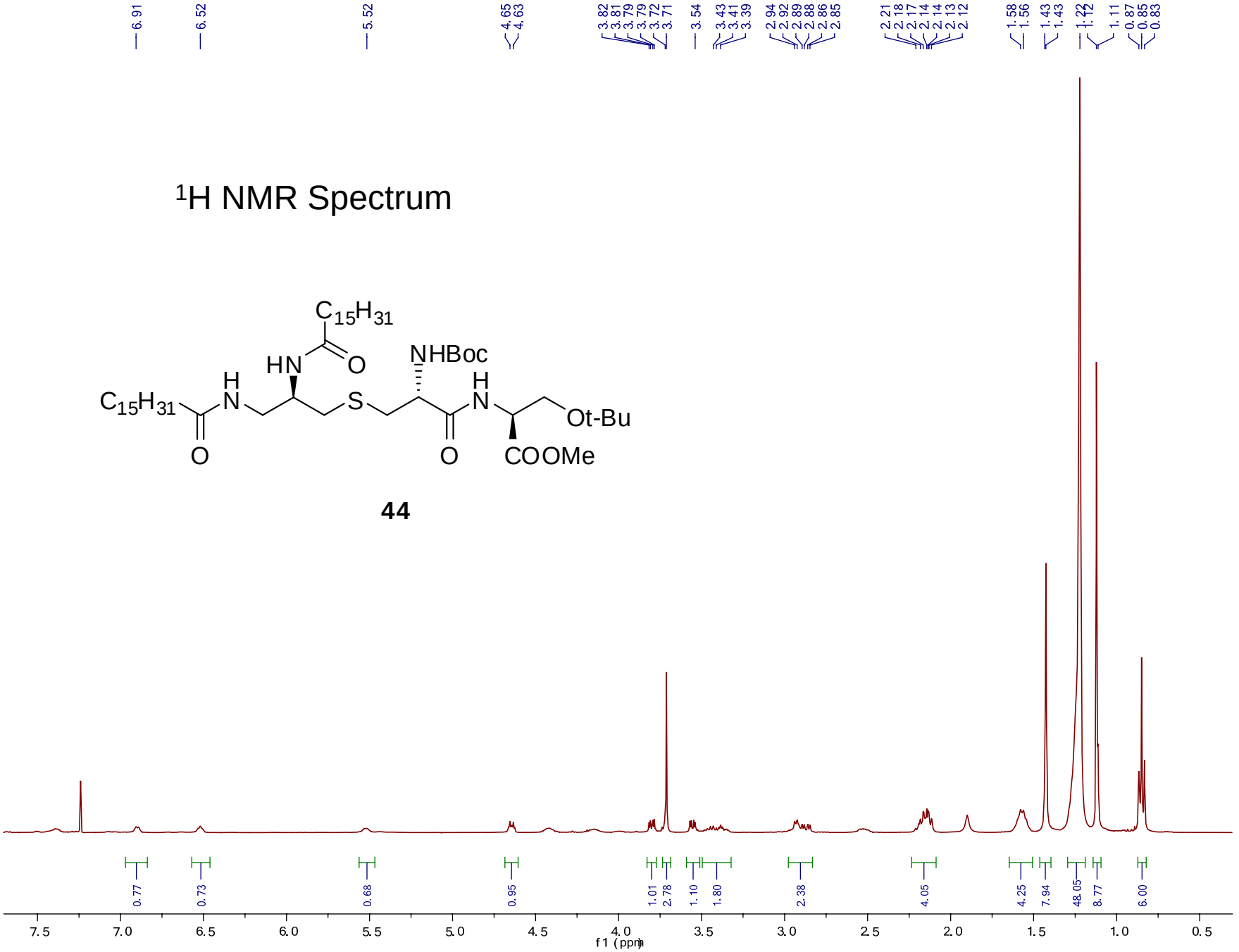


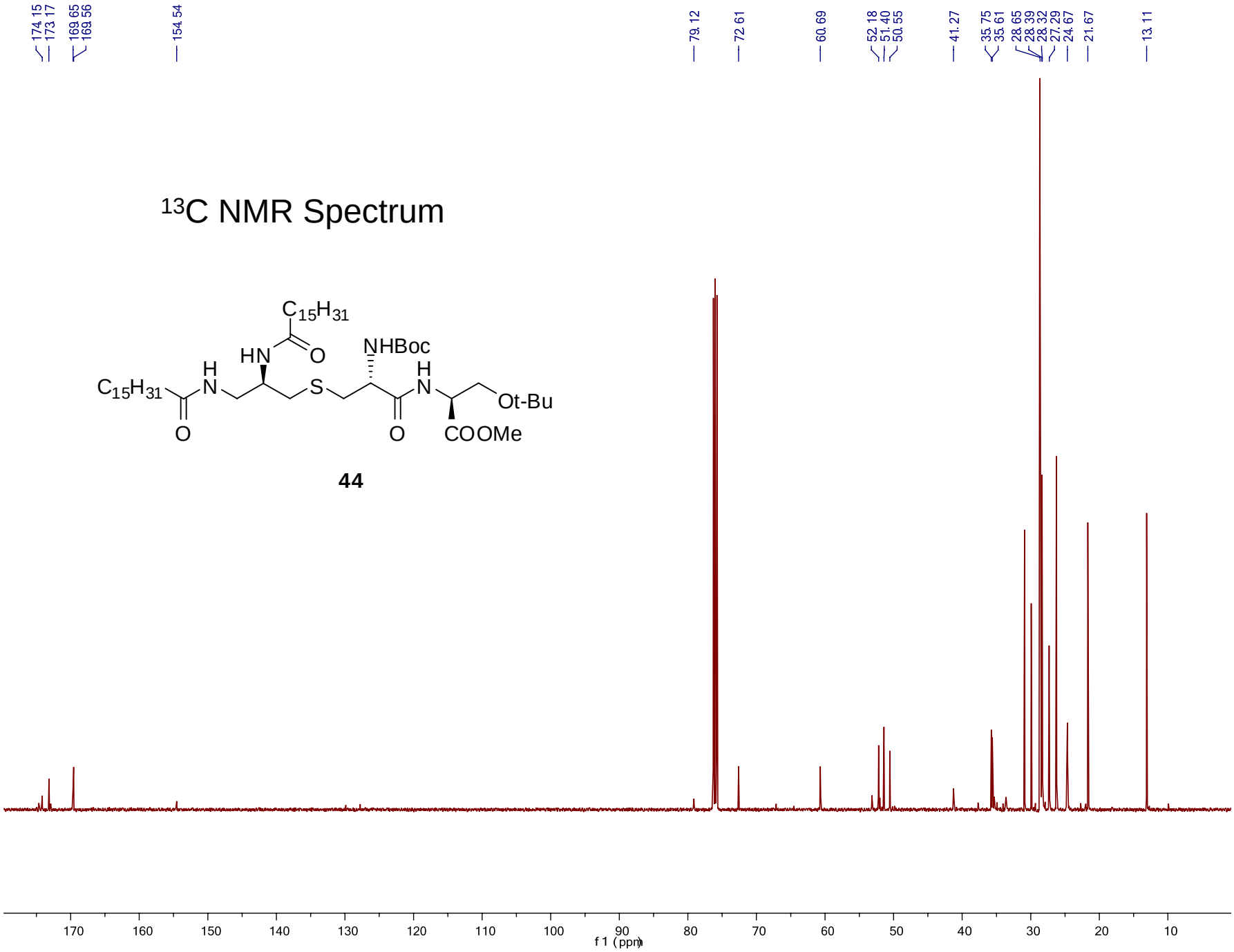

TOF Spectrum
TOF
Profile Spectrum at 1362.67 min (scan 1)
Baseline = 10.6506079376004
Abundance Min = 0
Abundance Max = 1408130
806.61391
807.61622
808.61641
Abundance
m/z
1.4M
1.2M
1.0M
0.8M
0.6M
0.4M
0.2M
0.0
500
600
700
800
900
1000
1100
1200
1300
1400
1500
C15H31
HN
O
NHBoc
H
N
S
O
O
C15H31
O

43

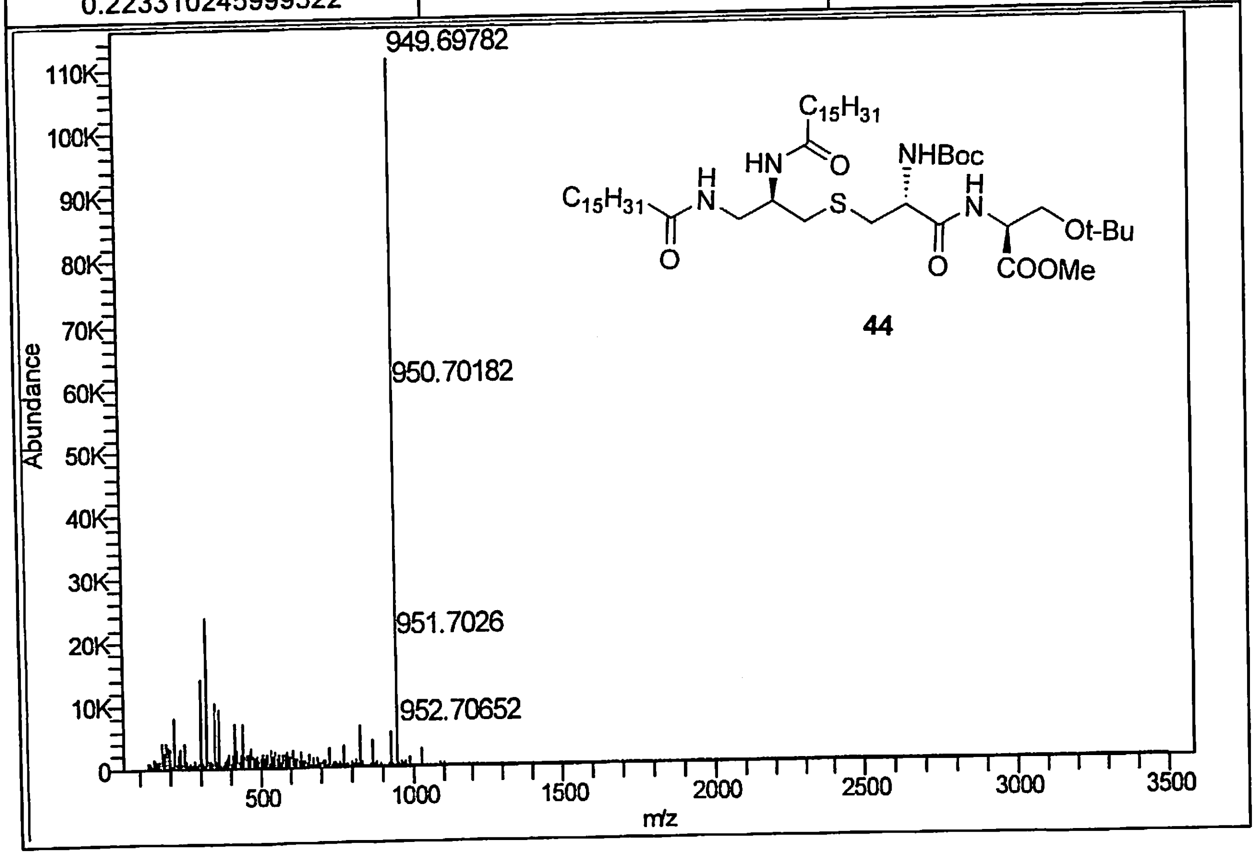
^{1}H NMR Spectrum

44



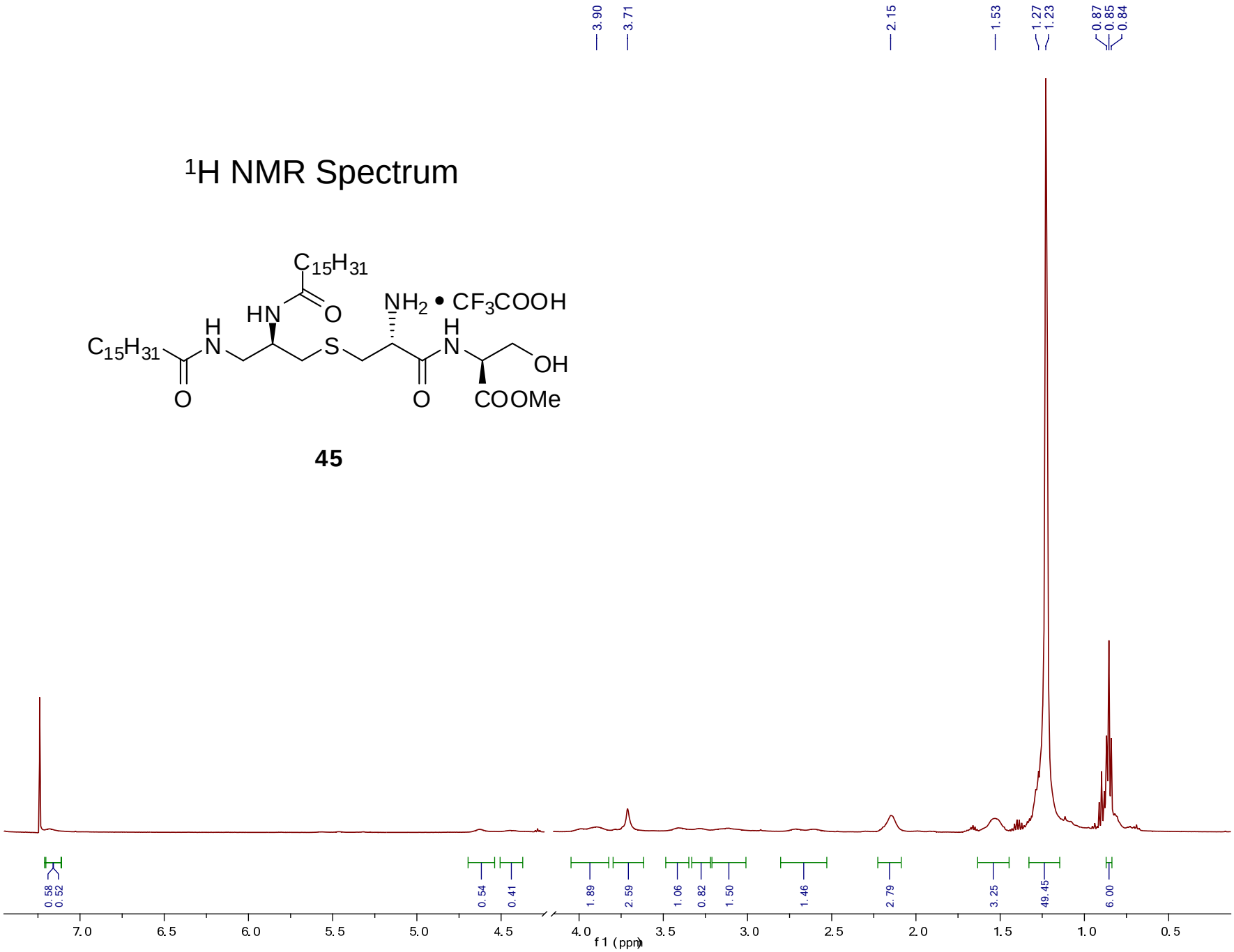

174.15
173.17
169.65
169.56
154.54
79.12
72.61
60.69
52.18
51.40
50.55
41.27
35.75
35.61
28.65
28.39
28.32
27.29
24.67
21.67
13.11
13C NMR Spectrum
C15H31
HN
O
NHBoc
H
N
C15H31
S
H
N
Ot-Bu
O
O
COOMe
44
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

TOF Spectrum	TOF	Profile Spectrum at 5712.72 min (scan 1)
Baseline = 0.223310245999522	Abundance Min = 0	Abundance Max = 111047



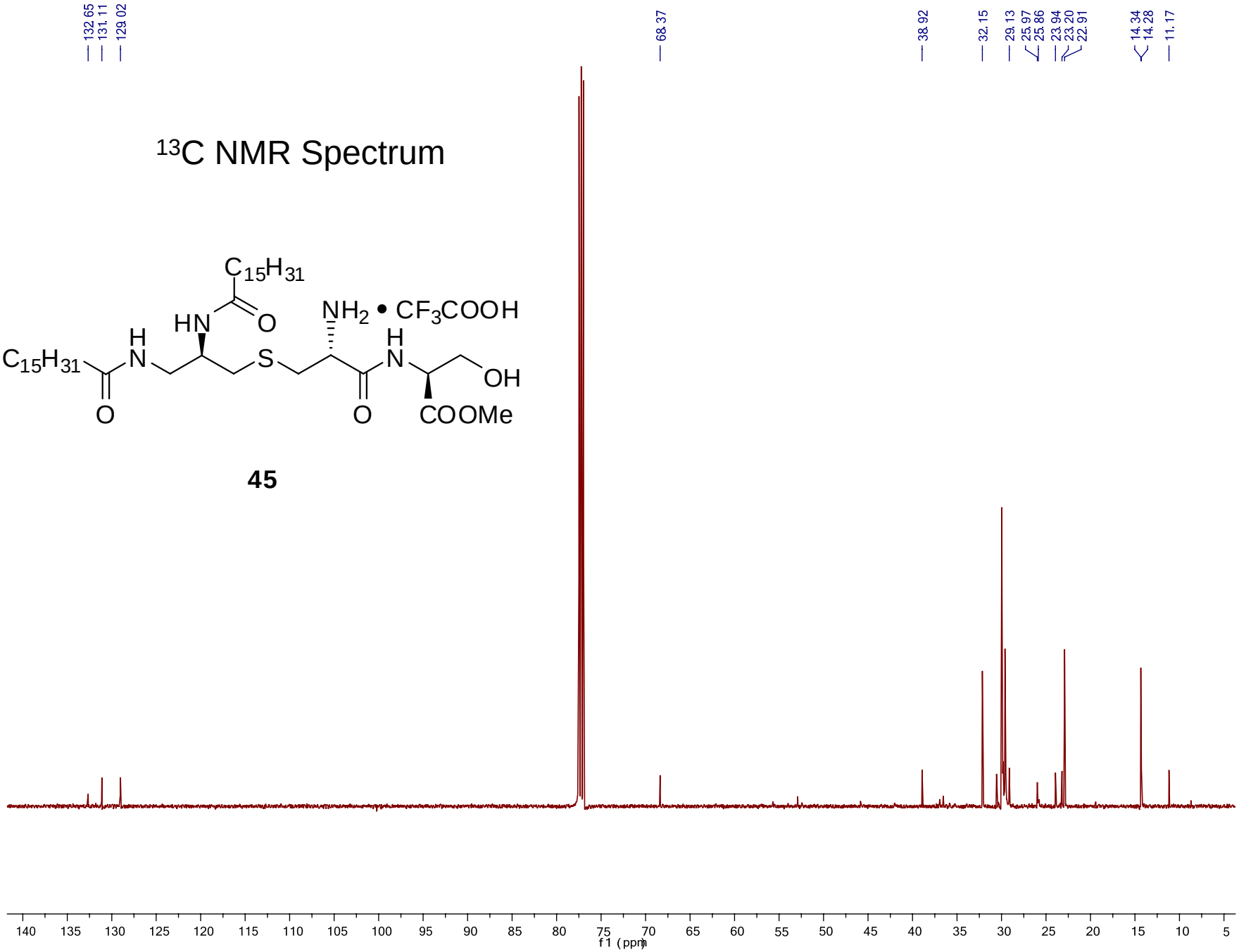
^{1}H NMR Spectrum

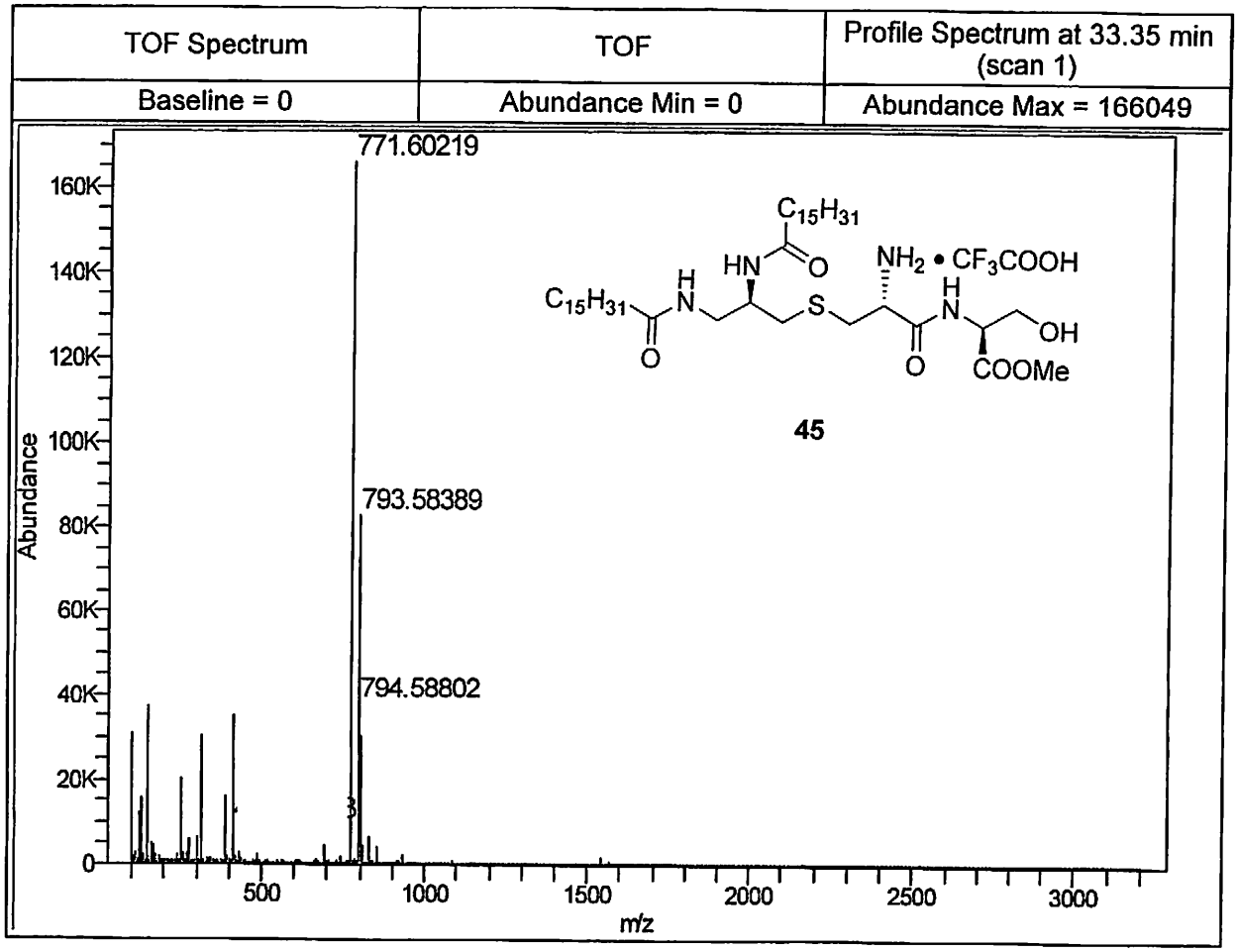
45



^{13}C NMR Spectrum

45




TOF Spectrum
TOF
Profile Spectrum at 33.35 min (scan 1)
Baseline = 0
Abundance Min = 0
Abundance Max = 166049
771.60219
793.58389
794.58802
Abundance
m/z
160K
140K
120K
100K
80K
60K
40K
20K
0
500
1000
1500
2000
2500
3000
C15H31
HN
O
NH2 • CF3COOH
H
N
S
OH
COOMe
45